THE UNIVERSITY OF ALBERTA

.FREE-RADICAL SUBSTITUTION REACTIONS OF SOME SULFENYL

CHLORIDES

BY

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The undersigned certify that they have read, and recommend

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TO   LINDA

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ABSTRACT

The free-radical substitution reactions of two sulfenyl chlorides, pentachlorobenzenesulfenyl chloride (PBSC) and sulfur monochloride were investigated with the intention of gaining insight into the mechanism of the substitution reactions of sulfenyl chlorides.

PBSC was previously reported to react with alkanes to give hydrogen chloride, alkyl chlorides, alkyl pentachlorophenyl sulfides and bispentachlorophenyl disulfide. In the present study, initiation of the reaction of PBSC with cyclohexane by azobisisobutyronitrile indicated a free-radical chain reaction of moderate chain length. Satisfactory material balances were established for the photoinitiated reactions of PBSC with cyclohexane, butane and isobutane. The apparent selectivity of the pentachlorophenylthiyl radical was deter-mined. The selectivity of PBSC toward primary, secondary and tertiary hydrogen atoms was found to be different from that of chlorine atoms or pentachlorophenylthiyl radicals. A chain mechanism is proposed for free-radical substitution reactions of PBSC in which both chlorine atoms and pentachlorophenylthiyl radicals are the chain carrying radicals.

Sulfur monochloride has been reported to undergo photoinitiated reaction with alkanes to give alkylthiosulfenyl chlorides (RSSCl) as isolable intermediates which could also undergo further reaction. In this work the photoinitiated reactions of sulfur monochloride with

alkanes were studied. By prolonged irradiation all intermediates reacted to give as the final products hydrogen chloride, alkyl chlorides, dialkyl polysulfides and elemental sulfur by a free-radical process. Efforts to determine if a chain reaction was occurring gave inconclusive results. For cyclohexane it was shown that cyclohexylthiosulfenyl chloride was not the sole reaction intermediate. The selectivity in hydrogen atom abstraction and relative reactivities observed for several hydrocarbons were the same for sulfur monochloride as for molecular chlorine. This suggests that chlorine atoms are responsible for hydrogen atom abstraction. The lack of evidence for a chain reaction and the complexity of the transformations of the reaction intermediates precluded the formulation of a complete reaction mechanism.

TABLE OF CONTENTS

LIST OF TABLES

INTRODUCTION

INTRODUCTION

The sulfenyl chlorides (RSCl) are a reactive class of compounds possessing a varied and interesting chemistry. A comprehensive review of sulfenyl halide chemistry for the period 1961-1965 is that of Kharasch, Ariyan and Havlik (1). This review also makes reference to other review articles on more specific topics, e.g., trichloromethanesulfenyl chloride and sulfur monochloride.

Mueller and Butler have stated that three modes of reaction are conceivable for sulfenyl chlorides (2).

$$RSCl \longrightarrow RS^{\oplus} + Cl^{\ominus} \qquad (1)$$

$$RSCl \longrightarrow RS^{\ominus} + Cl^{\oplus} \qquad (2)$$

$$RSCl \longrightarrow RS\cdot + Cl\cdot \qquad (3)$$
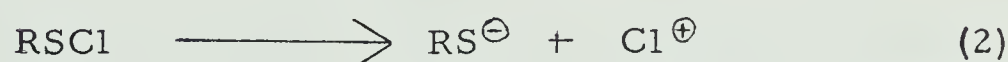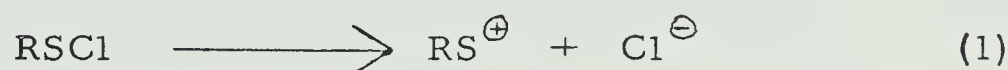
Bond breaking according to equation 1 is observed in the ionic addition of sulfenyl chlorides to olefins.* Heterolysis according to equation 2 is not yet a recognized reaction (2). Homolysis of the S-Cl bond (equation 3) has been well documented by a variety of free-radical reactions of sulfenyl chlorides (3-13).

The chain propagation steps are the product-determining reactions of a free-radical chain reaction. In free-radical substitution reactions with hydrocarbons, the first propagation step is generation of a radical $R\cdot$. This is usually accomplished by a hydrogen

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* Reference 2 contains an excellent account of the historical development of the mechanism of ionic addition of sulfenyl chlorides to olefins.

abstraction reaction.

$$RH \ + \ X\cdot \longrightarrow R\cdot \ + \ HX \qquad (4)$$

This is followed by chain transfer _via_ displacement of $R\cdot$ on XY to give the substitution product.

$$R\cdot \ + \ XY \longrightarrow RY \ + \ X\cdot \qquad (5)$$

In free-radical addition reactions hydrogen abstraction is replaced by addition of $X\cdot$ to a multiple bond, as in equation 6.

$$RCH = CH_2 \ + \ X\cdot \longrightarrow R\overset{\cdot}{C}H - CH_2X \qquad (6)$$
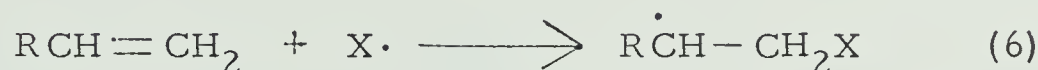
Inclusion of equation 5 completes the chain propagation sequence.

Radical displacement reactions (equations 4 and 5) usually occur on univalent atoms (14). When XY = RSCl, however, chain transfer can occur by displacement on either chlorine or sulfur (8, 11, 12, 13), generating either $RS\cdot$ or $Cl\cdot$ as the chain-carrying radical responsible for hydrogen atom abstraction or addition to a multiple bond.

In considering the free-radical substitution reactions of sulfenyl chlorides, therefore, one must consider hydrogen atom abstraction by either chlorine atoms or thiyl radicals, and chain transfer on either chlorine or sulfur.

The photochlorination of saturated hydrocarbons with molecular chlorine provides an example of both hydrogen abstraction by chlorine atoms,

$$RH \ + \ Cl\cdot \longrightarrow R\cdot \ + \ HCl \ ,$$

and radical displacement on chlorine

$$R\cdot \ + \ Cl-Cl \ \longrightarrow \ RCl \ + \ Cl\cdot$$

Chlorine atoms exhibit a high reactivity toward C-H bonds and therefore the selectivity is low* with respect to primary, secondary and tertiary hydrogen atoms (15). The primary : secondary : tertiary ratio for chlorine atoms at $40°$ is $1 : 3.6 : 4.2$ (16).

Equation 7 is a general representation of hydrogen abstraction by a thiyl radical.

$$-\overset{\displaystyle |}{\underset{\displaystyle |}{C}}-H \ + \ RS\cdot \ \underset{(7b)}{\overset{(7a)}{\rightleftharpoons}} \ -\overset{\displaystyle |}{\underset{\displaystyle |}{C}}\cdot \ + \ RSH \qquad (7)$$
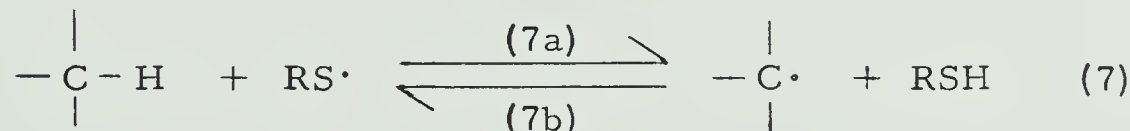
Equation 7b is hydrogen donation by RSH. Thiols are often excellent hydrogen donors. The chain transfer constant[‡] of butanethiol with styrene is 22 at $60°$, while the transfer constant for cyclohexane is 4×10^{-6} (17).

Walling has estimated the activation energy for chain transfer between a polystyryl radical and n-octanethiol as 6.5 kcal/mole (18).

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* The selectivity of a radical in hydrogen abstraction refers to the relative ease (relative rate) with which the radical is able to abstract a particular hydrogen atom. A primary : secondary : tertiary ratio of 1 : 10 : 100 for example, means that a tertiary hydrogen is abstracted 10 times faster than a secondary hydrogen which in turn is abstracted 10 times faster than a primary hydrogen.

‡ The chain transfer constant is obtained from polymerization data and is defined as the rate of chain transfer compared to the rate of polymerization.

Using a value of 77.5 kcal/mole for D(C-H) of a benzylic hydrogen atom and 86 kcal/mole for D(S-H) of a normal alkanethiol, he estimates an endothermicity of 8.5 kcal/mole for chain transfer (equation 7b). Within experimental error ($\pm$ 2 kcal/mole) the activation energy (E) and the enthalpy of reaction (ΔH) are the same. He concludes that there is little or no activation energy in excess of the energy requirements for chain transfer. Invoking microscopic reversibility, hydrogen atom abstraction by thiyl (equation 7a) should also have a low activation energy and be exothermic for the example above.

Carbon hydrogen bond energies for alkyl hydrogens range from 90 kcal/mole for tertiary C-H to 98 kcal/mole for primary C-H (19). Using D(S-H) = 86 kcal/mole, hydrogen atom abstraction reactions by thiyl radicals now become endothermic.

Walling concludes that the equilibrium represented by equation 7 will be a delicate one with small changes in structure influencing the direction of equilibrium (18). When the carbon radicals are resonance stabilized (e.g. benzylic or allylic), hydrogen abstraction by thiyl should be feasible.

Several experimental observations illustrate this point. Tetralin is dehydrogenated to naphthalene in 70% yield by heating with iso-amyl disulfide (20). Tetralin, 9,10-dihydroanthracene and phenylcyclohexane are dehydrogenated by phenyl disulfide at 260° (21). Generation of n-butanethiyl radicals by irradiating cumene solutions

of n-butyl disulfide at room temperature leads to n-butanethiol and bicumyl as the major products (22). Extension of the system to other hydrocarbons gives the following order of reactivity: cumene > ethylbenzene > toluene > isooctane > cyclohexane (22). Isooctane and cyclohexane react at a negligible rate. Similar results are obtained with iso-butyl- and t-butyl disulfide (23).

The photolysis of aromatic disulfides is complicated by rearrangements. Kooyman et al. have overcome this difficulty by using mesityl disulfide with the ortho and para positions blocked (24). Photolysis of this disulfide in the presence of 9,10-dihydroanthracene gave 2,4,6-trimethylthiophenol in 80% yield. Recently, van Zwet and Kooyman have been able to generate thiyl radicals by the thermal decomposition of arene diazothiolates (25). The 4-t-butylphenylthiyl radicals generated in this manner abstracted hydrogen from 9,10-dihydroanthracene but not from tetralin. t-Butylthiyl radicals generated in the same manner abstracted hydrogen from both donors.

Trotman-Dickenson and coworkers have studied the photo-decomposition of acetaldehyde in the vapor phase and in the presence of various thiols (26).

$$CH_3\overset{O}{\overset{\|}{C}}-H \;+\; RS\cdot \longrightarrow RSH \;+\; CH_3\overset{O}{\overset{\|}{C}}\cdot \qquad (9a)$$

$$CH_3\overset{O}{\overset{\|}{C}}\cdot \longrightarrow \cdot CH_3 \;+\; CO \qquad (9b)$$

$$\cdot CH_3 \;+\; RSH \longrightarrow CH_4 \;+\; RS\cdot \qquad (9c)$$
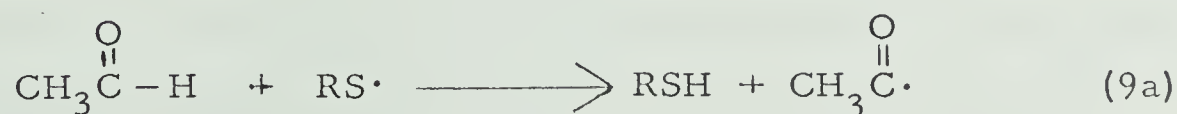
The catalytic effect represented by equation 9a decreases in

the order

$$R \ = \ H > CH_3 > C_2H_5 > \underline{iso}\text{-}C_3H_7 > \underline{t}\text{-}C_4H_9 \ ,$$
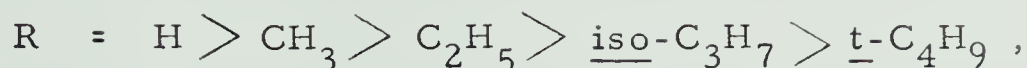
for the thiols, while the hydrogen donating ability represented by

equation 9c increases in the same order. These observations are

in agreement with those of Franklin and Lumpkin (27) who found that

D(S-H) decreases in the order

$$H-SH > H-SCH_3 > H-SC_2H_5 .$$
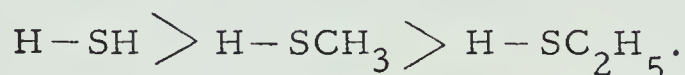
It is reasonable to assume that structural factors influence hydrogen

abstraction by thiyl radicals through an increase or decrease in the

S-H bond strength, although polar and steric effects cannot be

discounted.

A variety of radical displacement reactions on sulfur are

known (13, 28-32).

$$R-S-X \ + \ Y\cdot \ \longrightarrow \ R-S-Y \ + \ X\cdot$$
$$X \ = \ Cl, RS, \ -S\underset{x}{\cdot}(R = -S\cdot)$$
$$Y \ = \ R'\cdot , R'S\cdot , \ -S_xS\cdot$$
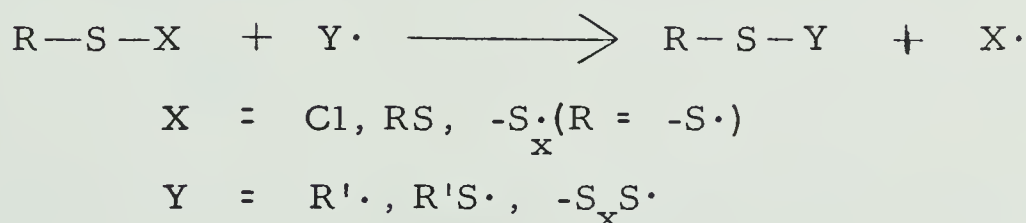
The variation in the viscosity of elemental sulfur with temper-

ature is attributed to the formation of high polymers. Polythiyl

radicals ($-S_xS\cdot$) undergo a rapid displacement reaction on S_8 rings to

increase the number of sulfur atoms in the polythiyl chain (33).

Disulfides exchange mercapto groups according to equations

10 and 11.

$$RSSR \ \underset{\text{initiator}}{\overset{\text{heat, light, or}}{\rightleftharpoons}} \ 2 \ RS\cdot \qquad\qquad (10)$$

$$RS\cdot \; + \; R'SSR' \xrightarrow{\hspace{2cm}} RSSR' \; + \; R'S\cdot \qquad (11)$$
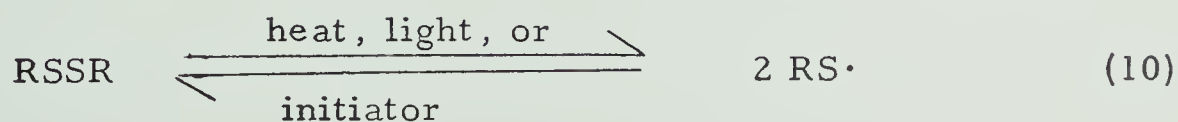
The reaction of N-bromosuccinimide with disulfides has been suggested to involve a radical displacement on sulfur by a succinimyl radical (29).
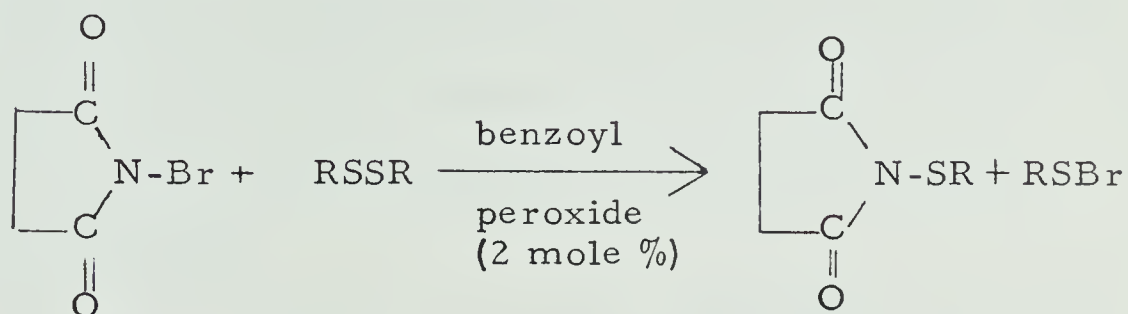
The key step in the photochemical conversion of 2-iodo-2'-methylthiobiphenyl into dibenzothiophene is an intramolecular displacement of the sulfur atom by the aryl radical (30).
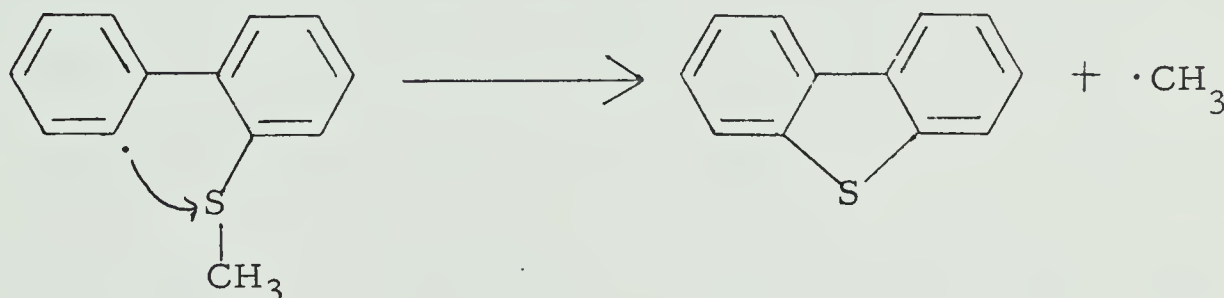
The mechanism proposed for the conversion of disulfides into sulfides by the action of trialkyl phosphites includes a displacement reaction by an alkyl radical on the S-S bond (31).

Pryor and Guard have studied the displacement by phenyl radicals on a series of alkyl disulfides (32). The phenyl radicals were generated by the thermal decomposition of phenylazotriphenyl-methane in carbon tetrachloride solution. Once generated, the phenyl radicals ($\phi\cdot$) could react in one of three ways:

$$RSSR + \phi\cdot \xrightarrow{k_1} RSSR'\cdot + \phi H$$

$$RSSR + \phi\cdot \xrightarrow{k_2} RS\phi + RS\cdot$$

$$CCl_4 + \phi\cdot \xrightarrow{k_3} \cdot CCl_3 + \phi Cl$$
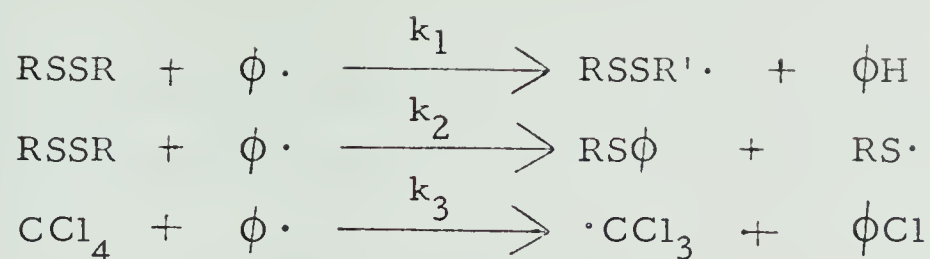
The ratio k_2/k_1 was determined for a series of disulfides and used to calculate the percentage attack on sulfur vs. attack on hydrogen. This varied from 98% with methyl disulfide to 49% with the more hindered t-butyl disulfide.

The free-radical reactions of some specific sulfenyl chlorides will now be considered.

Thiocyanogen chloride reacted photolytically with aralkyl hydrocarbons giving hydrogen chloride and aralkyl thiocyanates (3). The mechanism suggested by the authors for this reaction is:

$$ClSCN \xrightarrow{h\nu} Cl\cdot + \cdot SCN$$

$$Ar-\overset{|}{\underset{|}{C}}-H + Cl\cdot(\cdot SCN) \longrightarrow Ar-\overset{|}{\underset{|}{C}}\cdot + HCl\ (HSCN)$$

$$Ar-\overset{|}{\underset{|}{C}}\cdot + ClSCN \longrightarrow Ar-\overset{|}{\underset{|}{C}}-SCN + Cl\cdot$$
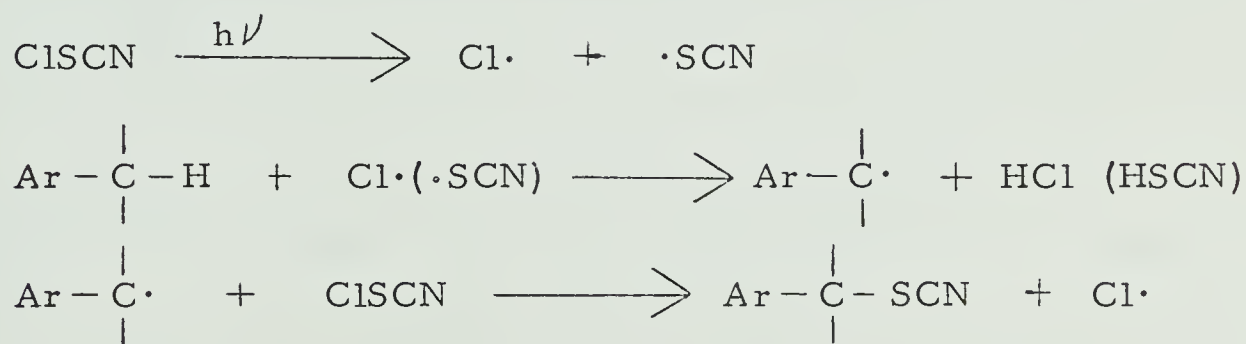
Their observations that t-butylbenzene was unreactive (3) and that thiocyanogen itself also gave photolytic thiocyanation (34) suggest a mixed chain where the following steps are included:

$$Ar-\overset{|}{\underset{|}{C}}-H + \cdot SCN \longrightarrow Ar-\overset{|}{\underset{|}{C}}\cdot + HSCN$$

$$HSCN + ClSCN \longrightarrow NCS-SCN + HCl$$

$$Ar-\overset{|}{\underset{|}{C}}\cdot + NCS-SCN \longrightarrow Ar-\overset{|}{\underset{|}{C}}-SCN + \cdot SCN$$
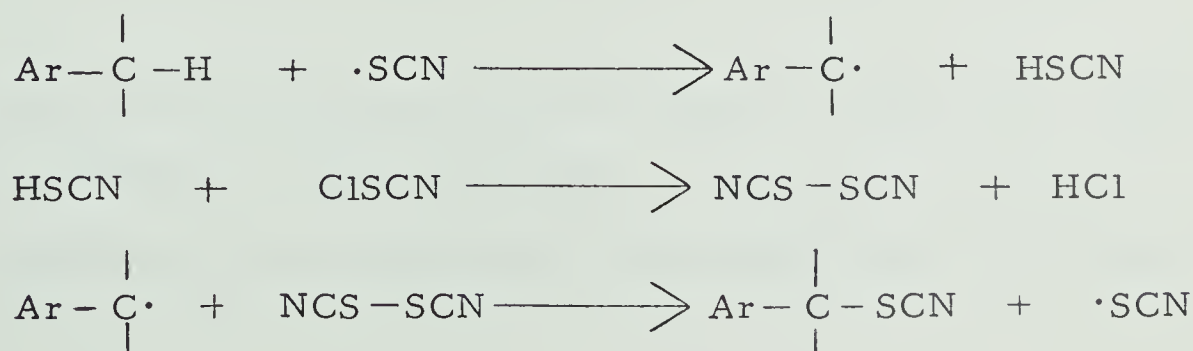
The free-radical substitution and addition reactions of tri-

chloromethanesulfenyl chloride (TCMSC) were first studied by Prey

and coworkers (4-6). Light or initiators such as benzoyl peroxide

catalyzed the addition of TCMSC to olefins (4). Further evidence for

the addition going by a free-radical pathway was the inhibition by

oxygen and nitric oxide (5). The orientation of the adduct with

styrene was established by infrared spectroscopy (5). This orient-

$$\text{(styrene)} \ + \ Cl_3SCl \ \longrightarrow \ \text{(adduct with SCCl}_3 \text{ and Cl)} \qquad (12)$$
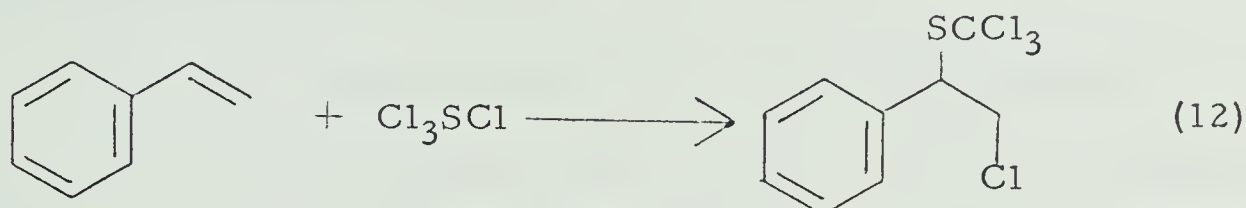
ation suggests that Cl· is the adding species; the resulting styryl

radical undergoes chain transfer with Cl_3CSCl to give the adduct with

the orientation shown.

$$\text{(styrene)} \ + \ Cl· \ \longrightarrow \ \text{(radical with Cl)} \qquad (12a)$$

$$\text{(radical with Cl)} \ + \ Cl_3CSCl \ \longrightarrow \ \text{(adduct with SCCl}_3 \text{ and Cl)} + Cl· \qquad (12b)$$
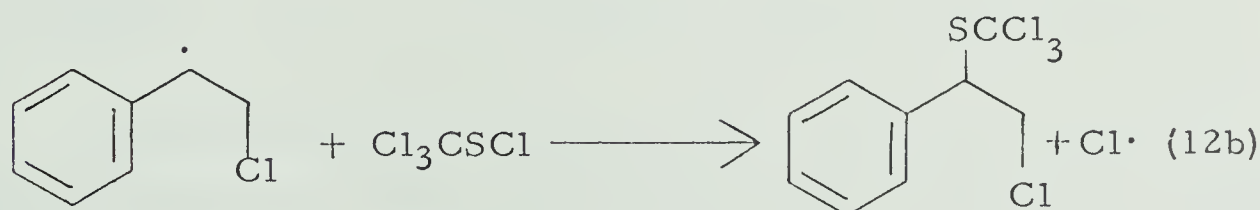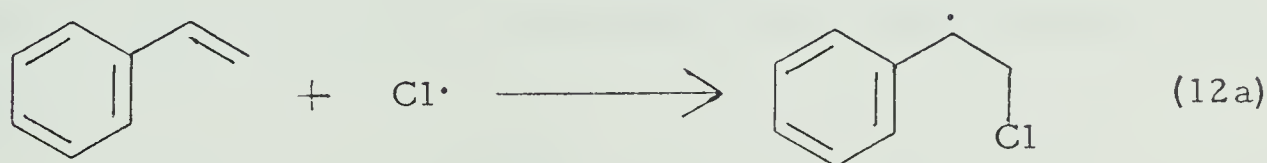
This observation is in conflict with the results of later work. The

addition of TCMSC to phenyl vinyl ether proceeded thermally, or

under catalysis by benzoyl peroxide or ultraviolet light to give the

product shown below (35).
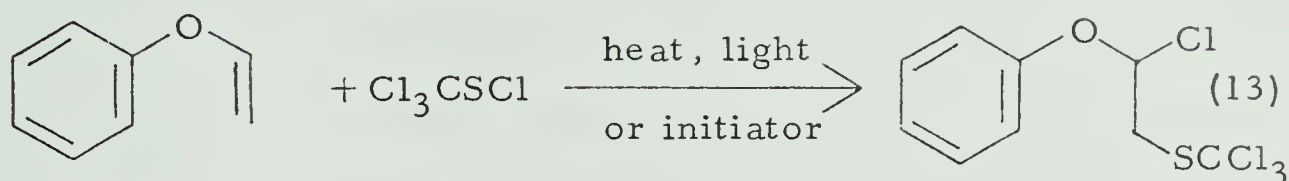
A trace of the product with the reverse orientation was observed in the thermal reaction.

This work suggests that $Cl_3CS\cdot$ is the adding radical. Kloosterziel has also expressed the view that in addition reactions of TCMSC, $Cl_3CS\cdot$ is the adding species (8, 36). Kharasch, Ariyan and Havlik (37) have suggested that the structural assignment of the adduct from TCMSC and styrene may merit revision.

Equation 14 is the reaction of TCMSC with saturated hydrocarbons (6). A mixed chain was proposed which included both chlorine atoms and trichloromethylthiyl in the hydrogen abstraction steps.

$$2 \, Cl_3CSCl \, + \, RH \, \xrightarrow{h\nu} \, RCl \, + \, HCl \, + \, Cl_3CSSCCl_3 \quad (14)$$
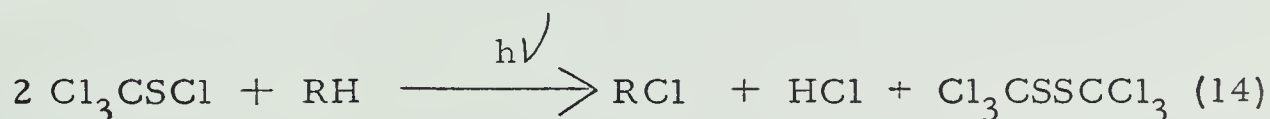
The photoinitiated reaction of other sulfenyl chlorides (alkyl, aryl and 2-nitroaryl) with cyclohexane has been followed by evolution of hydrogen chloride and yield of the corresponding disulfide (7). The alkyl and aryl sulfenyl chlorides were found to be more reactive than the 2-nitroaryl sulfenyl chlorides.

A later study by Kloosterziel (8) established the exact

stoichiometry of equation 14. From the selectivity observed (ca. 1 : 30 : 110 for the primary, secondary and tertiary hydrogens of n-pentane and 2,3-dimethylbutane) and the large deuterium isotope effect ($k_H/k_D = 1.9 \pm 0.1$), he concluded that a very selective radical was responsible for hydrogen atom abstraction. Complexation of chlorine atoms with TCMSC itself or with bistrichloromethyl disulfide to give a stabilized, more selective species was ruled out. Thiophosgene was not an intermediate. Kloosterziel proposed the mechanism shown below.

$$Cl_3CSCl \xrightarrow{h\nu} Cl_3CS\cdot \ + \ Cl\cdot$$

$$Cl_3CS\cdot + RH \longrightarrow Cl_3CSH \ + \ R\cdot$$

$$R\cdot \ + \ Cl_3CSCl \longrightarrow Cl_3CS\cdot \ + \ RCl$$

$$Cl_3CSCl \ + \ Cl_3CSH \longrightarrow Cl_3CSSCCl_3 \ + \ HCl$$
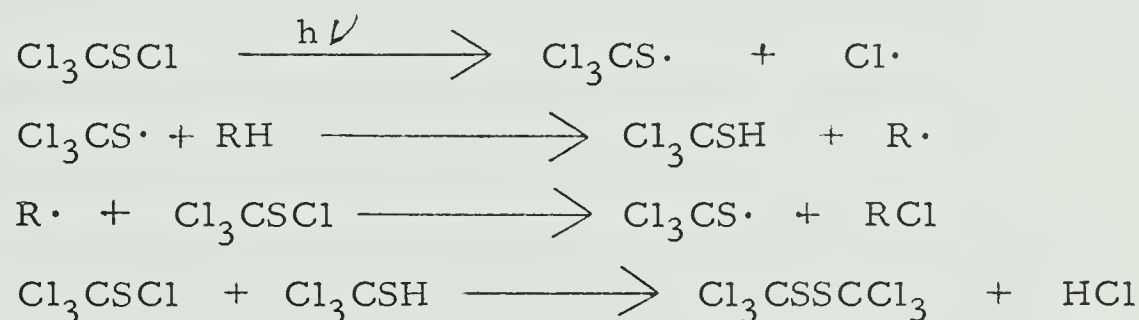
The high selectivity ruled out any significant participation in the chain by chlorine atoms.

Harris has carried out a comprehensive study of the free-radical addition of trifluoromethanesulfenyl chloride (TFMSC) to negatively substituted olefins (12). The addition goes by a mixed chain with chlorine atoms being the predominant adding species instead of $F_3CS\cdot$.

Later work by Harris describes the free-radical substitution reactions of TFMSC with hydrocarbons (13). Both alkyl chlorides and alkyl trifluoromethyl sulfides were obtained in addition to hydrogen chloride and bistrifluoromethyl disulfide. Initiation of the reaction

by 0.22 mole % of azobisisobutyronitrile established it as being a long chain process. The selectivities observed were primary : secondary 1 : 6 (n-butane) and primary : tertiary 1 : 39 (isobutane). Because of the selectivity and the products isolated, Harris proposed a mixed chain with Cl· and $F_3CS·$. Furthermore, the occurrence of the alkyl trifluoromethyl sulfides as reaction products (in addition to alkyl chlorides) was explained by a chain transfer step where displacement occurs either on sulfur (preferred) or on chlorine. The relative amount of sulfide increased in going from a tertiary to a secondary to a primary to a primary benzylic radical. This trend he explained as being due to a steric effect. He also attributed the differing behavior of TFMSC and TCMSC to a steric effect.

> "The difference in the behavior of F_3CSCl and Cl_3SCl in reactions with cyclohexane can also be attributed to steric effects; i.e., the sulfur atom in Cl_3CSCl is less easily attacked by the cyclohexyl radical because of the greater size of the adjacent trichloro-methyl group, and consequently attack on Cl_3CSCl occurs only at the chlorine atom."*

From the brief outline above, it is apparent that the free-radical chemistry of sulfenyl chlorides presents some topics of interest which merit further study. Namely: the factors influencing alkyl hydrogen atom abstraction by thiyl radicals, and the nature of radical displacement reactions of the S-Cl bond of sulfenyl chlorides. The answer to these questions is essential to the establishment of any detailed mechanism for the free-radical substitution reactions of sulfenyl chlorides.

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* Quotation taken from page 933 of reference 13.

Two sulfenyl chlorides were chosen for study: pentachloro-benzenesulfenyl chloride and sulfur monochloride.   Previous work on these two sulfenyl chlorides (11 and 10) had left the mechanisms of reaction unclear.   This present study was directed toward the clarification of these mechanisms.

PART   ONE

PENTACHLOROBENZENESULFENYL CHLORIDE

INTRODUCTION

Pentachlorobenzenesulfenyl chloride (PBSC) was first prepared by Putnam and Sharkey (38). Kharasch and Ariyan found that it readily underwent reaction with cyclohexane in diffuse sunlight but not in the dark, implying a free-radical process (11). The products they obtained (no yields reported) were: hydrogen chloride, bispentachlorophenyl disulfide, cyclohexyl chloride and cyclohexyl pentachlorophenyl sulfide. With toluene, side chain substitution occurred, the mixed sulfide being the major product. Kharasch and Ariyan proposed the following series of reactions to explain the products that they obtained.

$$ArSCl \quad \underset{\longleftarrow}{\overset{h\nu}{\rightleftharpoons}} \quad ArS\cdot \;+\; Cl\cdot \tag{1}$$

$$ArS\cdot \;+\; RH \;\longrightarrow\; ArSH \;+\; R\cdot \tag{2}$$

$$R\cdot \;+\; ArSCl \begin{cases} \longrightarrow ArSR \;+\; Cl\cdot & (3a) \\ \longrightarrow RCl \;+\; ArS\cdot & (3b) \end{cases}$$

$$RH \;+\; Cl\cdot \;\longrightarrow\; HCl \;+\; R\cdot \tag{4}$$

$$ArSH \;+\; ArSCl \;\longrightarrow\; ArSSAr \;+\; HCl \tag{5}$$
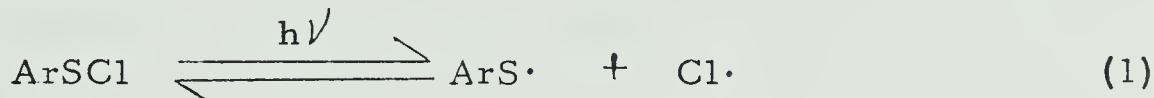
Their results left some questions unanswered. The chain nature of the reaction was not established nor was the selectivity of the abstracting species determined. Also product yields were lacking so the possibility of other reaction products could not be excluded.

The above proposal was reasonable in view of the products obtained. However, alternative possibilities might have explained

these products equally well. The four reaction schemes outlined below were considered as other possible explanations. Underlined products are those obtained by Kharasch and Ariyan.

SCHEME I

$$ArSCl \xrightarrow{h\nu} ArS\cdot + Cl\cdot$$

$$Cl\cdot + RH \longrightarrow \underline{HCl} + R\cdot$$

$$R\cdot + ArSCl \longrightarrow \underline{RCl} + ArS\cdot$$

$$R\cdot + ArSCl \longrightarrow \underline{ArSR} + Cl\cdot$$

$$R\cdot + ArSSAr \longrightarrow \underline{ArSR} + ArS\cdot$$

$$ArSCl + HCl \rightleftharpoons ArSH + Cl_2$$

$$ArSH + ArSCl \longrightarrow \underline{ArSSAr} + HCl$$

$$2\ ArS\cdot \longrightarrow \underline{ArSSAr}$$

SCHEME II

$$ArSCl \xrightarrow{h\nu} ArS\cdot + Cl\cdot$$

$$Cl\cdot + RH \longrightarrow \underline{HCl} + R\cdot$$

$$R\cdot + ArSCl \longrightarrow \underline{RCl} + ArS\cdot$$

$$R\cdot + ArSCl \longrightarrow \underline{ArSR} + Cl\cdot$$

$$R\cdot + ArSSAr \longrightarrow \underline{ArSR} + ArS\cdot$$

$$ArS\cdot + ArSCl \rightleftharpoons \underline{ArSSAr} + Cl\cdot$$

$$2\ ArS\cdot \longrightarrow \underline{ArSSAr}$$

SCHEME III

$$ArSCl \xrightarrow{h\nu} ArS\cdot + Cl\cdot$$

$$ArS\cdot + RH \rightleftharpoons ArSH + R\cdot$$

$$R\cdot + ArSCl \longrightarrow \underline{RCl} + ArS\cdot$$

$$R\cdot + ArSCl \longrightarrow \underline{ArSR} + Cl\cdot$$

$$R\cdot + ArSSAr \longrightarrow \underline{ArSR} + ArS\cdot$$

$$ArSH + ArSCl \longrightarrow \underline{ArSSAr} + \underline{HCl}$$

$$Cl\cdot + ArSSAr \rightleftharpoons ArSCl + ArS\cdot$$

$$2 ArS\cdot \longrightarrow \underline{ArSSAr}$$

SCHEME IV

$$ArSCl \xrightarrow{h\nu} ArS\cdot + Cl\cdot$$

$$Cl\cdot + RH \longrightarrow \underline{HCl} + R\cdot$$

$$ArS\cdot + RH \rightleftharpoons ArSH + R\cdot$$

$$R\cdot + ArSCl \longrightarrow \underline{RCl} + ArS\cdot$$

$$R\cdot + ArSCl \longrightarrow \underline{ArSR} + Cl\cdot$$

$$R\cdot + ArSSAr \longrightarrow \underline{ArSR} + ArS\cdot$$

$$ArSH + ArSCl \longrightarrow \underline{ArSSAr} + \underline{HCl}$$

$$2 ArS\cdot \longrightarrow \underline{ArSSAr}$$

Scheme IV was the same series of reactions proposed by
Kharasch and Ariyan except for the addition of one more chain transfer
reaction,

$$R\cdot \ + \ ArSSAr \ \longrightarrow \ \underline{ArSR} \ + \ ArS\cdot$$

and a termination reaction.

$$2 \ ArS\cdot \ \longrightarrow \ ArSSAr$$

The chain transfer reaction was included because of precedent (31, 32) for displacement reactions by alkyl radicals on disulfides. The termination reaction was considered to be the most likely termination reaction in view of the relative stability of thiyl radicals. These two reactions were included in all four of the reaction schemes for generality.

At the outset of this study, an estimation of the chain length for the reaction of PBSC with hydrocarbons was considered essential if any chain sequence was to be considered as a mechanism. As well, the selectivity of PBSC was required in order to decide between a scheme involving chlorine atoms (Schemes I and II), or pentachloro-phenylthiyl radicals (Scheme III), or both chlorine atoms and penta-chlorophenylthiyl radicals (Scheme IV), as the chain carrying radical(s). Material balances were required in order to ensure that the product distributions included all of the products of the reactions and that meaningful selectivities could be calculated for the chain carrying radical(s) from these product distributions.

This section describes the efforts made toward a better understanding of the mechanism of the photoinitiated substitution reactions of PBSC with saturated hydrocarbons.

R E S U L T S

I.   INITIATION-INHIBITION STUDIES

Kharasch and Ariyan (11) found that sunlight was an effective initiator for the reaction of PBSC with cyclohexane. The effect of inhibitors on this photoinitiated reaction was studied in addition to initiation by small amounts of a radical initiator AIBN.[‡] The results in Table I were obtained by studying reactions between PBSC (0.2 M) and cyclohexane (3.7 M) carried out in sealed Pyrex ampoules using carbon tetrachloride as solvent. The progress of the reactions could conveniently be followed by iodometric titration for unreacted PBSC.

The inhibition experiments were done in a Rayonet merry-go-round apparatus to ensure uniform irradiation of all the ampoules. The results in Table I showed that the reaction was not strongly inhibited by atmospheric amounts of oxygen or a few mole % of sym-trinitrobenzene. The use of other inhibitors such as amines, phenols, thiols or thiophenols was not pursued because sulfenyl chlorides react with these compounds.

Trace initiation by AIBN showed the reaction to have a moderate chain length in the vicinity of 40-100 as calculated from the results of Table I for initiation experiments.[*] Therefore, no more than 2-3

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[*] Chain lengths were calculated by assuming an efficiency of 50% for the initiator (see reference 14, page 132). The half-lives of AIBN at 40° and 71° were taken from reference 18, page 469.

[‡] AIBN = azobisisobutyronitrile.

per cent of the products could have arisen from termination (coupling) reactions and radical displacement reactions must have accounted for the remainder of the (substitution) products.

TABLE I

THE EFFECTS OF FREE-RADICAL INITIATORS AND INHIBITORS ON THE REACTION BETWEEN PBSC AND CYCLOHEXANE.

Conditions	Time, hr	Per cent Reaction
Degassed, 40°, hν	1.0	87
Degassed, 40°, hν, plus sym-trinitrobenzene[a]	1.0	81 82
Not degassed, 40°, hν	1.0	78 80
	2.0	91 93
Degassed, 40°, dark	333	4 6
Degassed, 40°, dark, plus AIBN (10 mole %)	98	86
	333	98 98
Degassed, 71°, dark	25	5 4
Degassed, 71°, dark, plus AIBN (2 mole %)	25	90 89

[a] Saturated solution, $\leqslant$ 5 mole % of PBSC.

The slow thermal reaction (dark reactions at 40° and 71°) indicated a slow thermal dissociation of PBSC into radicals. For

this reason, freshly prepared PBSC was used for all work in this
study.

II.   PHOTOINITIATED REACTION OF PBSC WITH CYCLO-
       HEXANE.

As found previously by Kharasch and Ariyan (11) PBSC under-
went photoinitiated reaction with cyclohexane to give hydrogen chloride,
bispentachlorophenyl disulfide, cyclohexyl chloride and cyclohexyl
pentachlorophenyl sulfide.   Hexachlorobenzene was the only product
not previously reported which could be found and identified.   Penta-
chlorothiophenol was present in only trace amounts.

ArSCl + [cyclohexane] $\xrightarrow[\text{CCl}_4,\ 40^\circ]{\text{h}\nu}$ HCl + ArSSAr + [cyclohexyl chloride, Cl]

I   II

+ [cyclohexyl SAr] + ArCl

III   IV
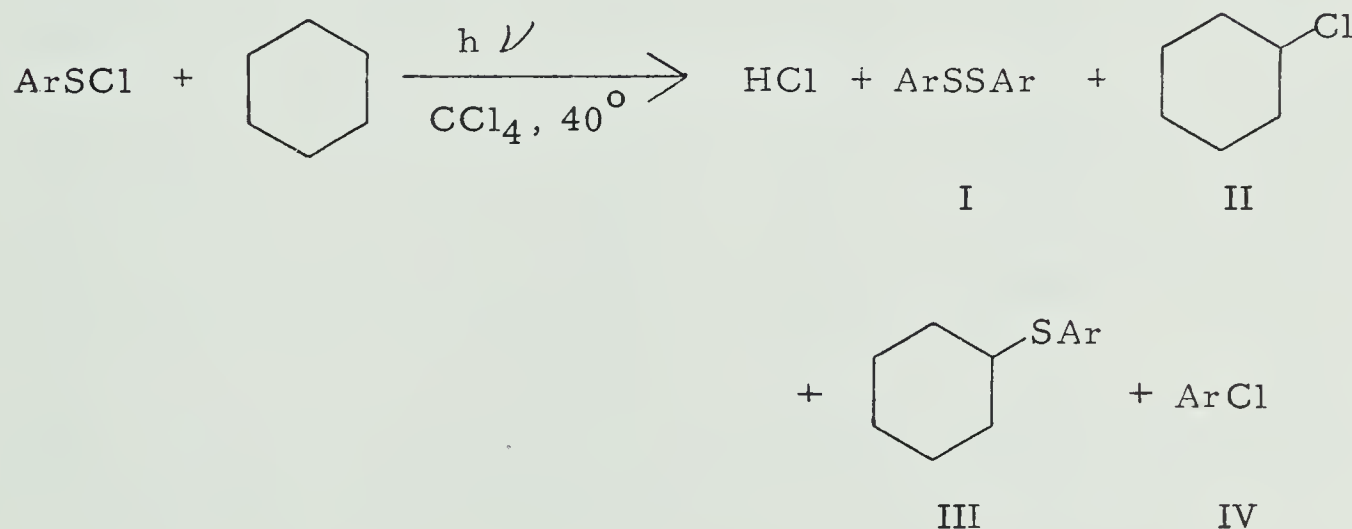
At 40° under our reaction conditions (0.3 M in PBSC, 3.7 M
in hydrocarbon, irradiation in sealed, degassed Pyrex ampoules),
the disulfide (I) crystallized out almost quantitatively by completion
of reaction (5-10 hr).   At 80° the reaction mixtures were homogeneous
throughout the entire reaction and the disulfide crystallized out after
the ampoules were cooled.   After analysis by glpc* for cyclohexyl

* Abbreviation used for gas liquid partition chromatography.

TABLE II

PRODUCT YIELDS IN THE PHOTOINITIATED REACTION OF PBSC

WITH CYCLOHEXANE.

Run[a]	HCl	I	II	III[b]	IV
		Yield, mole/mole PBSC			
1	0.75				
2	0.73				
3		0.19	0.17	0.64	
4		0.19	0.18	0.62	0.02
5		0.20	0.19	0.62	0.03
6		0.18	0.16	0.63	0.03
7		0.19	0.17	0.64	0.03
8		0.30	0.16	0.52	0.02
9		0.30	0.16	0.53	0.02
10			0.19	0.61	0.01

[a] All runs were at 40°, except runs 6 and 7 at 80°; all runs were 0.3 M in PBSC (1.48-1.56 mmole in 5.0 ml); runs 3-10 were 0.12 M in Freon 112 as internal standard; runs 8 and 9 were 0.04 M in pentachlorothiophenol. Run 10 was carried to 75% completion, analyzed and the yields corrected to 100% reaction.

[b] Calculated from the crude yield of the sulfide minus the yield of hexachlorobenzene.

chloride (Freon 112 internal standard), the disulfide was collected and weighed. Evaporation of the filtrate gave the remainder of the products as a white solid. This solid had the following composition: cyclohexyl pentachlorophenyl sulfide (90-95%), hexachlorobenzene (2-5% estimated by glpc), I (2-3% by isolation), a compound V $C_6Cl_5SC_6H_{10}Cl$ and/or $C_6Cl_5SC_6H_{11}S$ (small amounts estimated from the mass spectrum) and traces (ca. 0.2%) of pentachlorothiophenol. The thiophenol was analyzed as the acetate due to difficulties encountered in analyzing for it directly by glpc.

The yield of II, III and IV showed little variation with reaction temperature (runs 6 and 7 at 80°) or with the extent of reaction (run 10 stopped at 75% reaction). The material balance calculated for the reaction at 40° was as follows: 92% of the sulfenyl chloride chlorine could be found as hydrogen chloride and cyclohexyl chloride; 102% of the pentachlorophenylthio groups appeared as cyclohexyl penta-chlorophenyl sulfide and bispentachlorophenyl disulfide.

III. PHOTOINITIATED REACTION OF PBSC WITH NORMAL BUTANE AND ISOBUTANE.

Normal butane and isobutane were reacted with PBSC in order to determine the selectivity of the reagent from the product distribut-ions. Degassed solutions of PBSC (0.2 M) and hydrocarbon (3.3 M) in carbon tetrachloride were irradiated at 40° in sealed Pyrex ampoules. The products obtained were analogous to those from the cyclohexane reactions. Less than 0.5% of pentachlorothiophenol

(analyzed as the acetate) was produced in these reactions.

$$ArSCl \; + \; CH_3CH_2CH_2CH_3 \xrightarrow[CCl_4, \; 40^o]{h\nu} \; HCl \; + \; ArSSAr$$

$$+ \; CH_3CH_2CH_2CH_2Cl$$

$$+ \; CH_3CH_2CHClCH_3$$

$$+ \; ArS - CH_2CH_2CH_2CH_3$$

VIII

$$+ \; ArS - \overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2CH_3$$

IX

$$+ \; ArCl$$

$$ArSCl \; + \; H_3C - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - CH_3 \xrightarrow[CCl_4, \; 40^o]{h\nu} \; HCl \; + \; ArSSAr$$

$$+ \; H_3C - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - CH_2Cl$$

$$+ \; H_3C - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}} - CH_3$$

$$+ \; ArS - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - CH_3$$

X

$$+ \; ArS - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_3$$

XI

$$+ \; ArCl$$
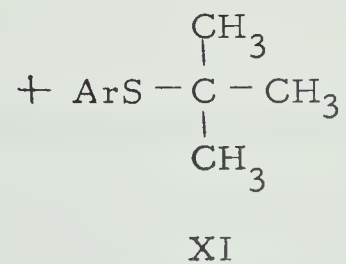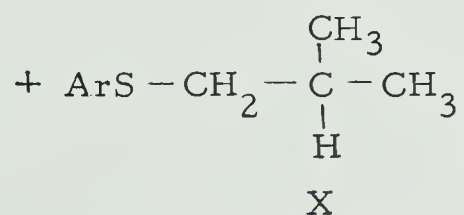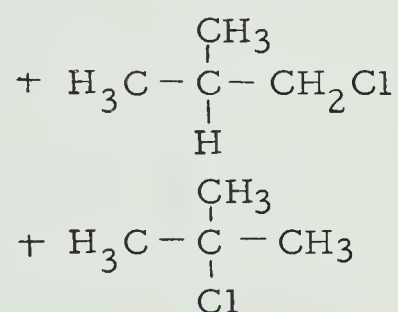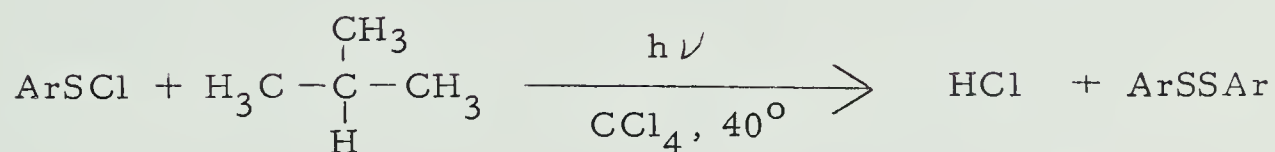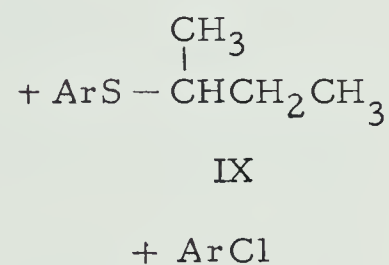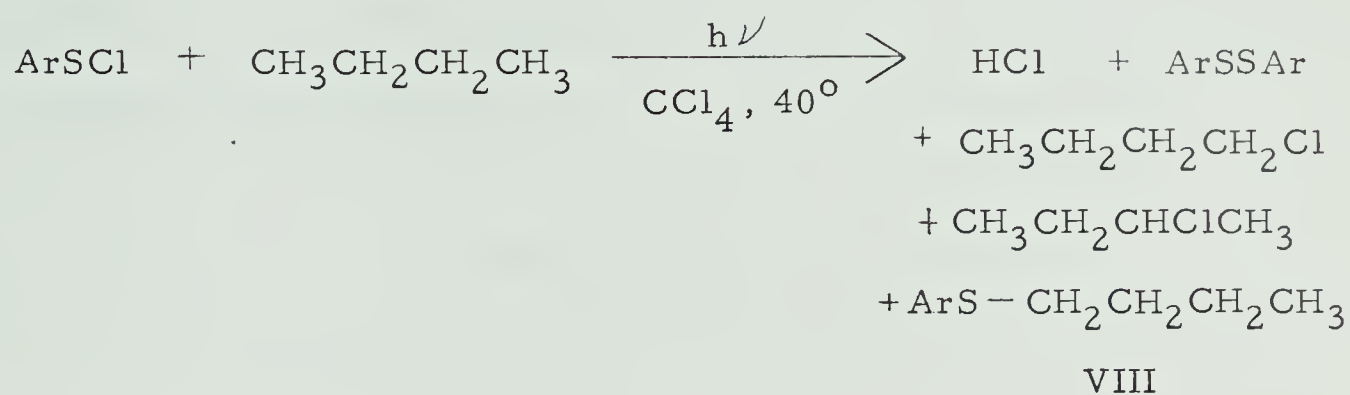
TABLE III

PRODUCT YIELDS IN THE PHOTOINITIATED REACTION OF PBSC

WITH NORMAL BUTANE AND WITH ISOBUTANE AT 40°.

mole product/mole of PBSC

	Butane		Isobutane		
	Run 11	Run 12	Run 13	Run 14	
$\underline{n}$-C_4H_9Cl	0.003	0.003	0.01	0.01	$\underline{iso}$-C_4H_9Cl
$\underline{sec}$-C_4H_9Cl	0.10	0.10	0.15	0.16	$\underline{t}$-C_4H_9Cl
VIII	0.13	0.13	0.19	0.18	X
IX	0.58	0.58	0.39	0.39	XI
C_6Cl_6	0.03	0.03	0.04	0.03	C_6Cl_6
$(C_6Cl_5S)_2$	0.15	0.16	0.20	0.20	$(C_6Cl_5S)_2$
primary : secondary selectivity	1 : 7.7	1 : 7.7	1 : 24.3	1 : 26.1	primary : tertiary selectivity

For butane the selectivity was calculated from the yield of secondary chloride and sulfide relative to the yield of primary chloride and sulfide times a statistical factor of 1.5. The selectivity with isobutane was calculated in the same way using a statistical factor of 9.

The yields and selectivities are presented in Table III. The material balance for these reactions was calculated indirectly by assuming one mole of hydrogen chloride for one mole of alkyl chloride or alkyl pentachlorophenyl sulfide. The material balances thus obtained were identical to that obtained for the cyclohexane reactions. The values calculated were 90-92% for chlorine and 97-103% for pentachlorophenylthio groups.

IV.   EFFORTS TO DETERMINE IF COMPLEXED CHLORINE
       ATOMS WERE INVOLVED IN HYDROGEN ABSTRACTION.

PBSC displayed a primary : secondary : tertiary selectivity of 1 : 8 : 25 at 40° which was substantially more selective than molecular chlorine for which a primary : secondary : tertiary selectivity of 1 : 3.6 : 4.2 at 40° has been reported (16).

Complex formation between chlorine atoms and molecules of PBSC or one of the products to give a stabilized and therefore more selective species was considered as one explanation of the enhanced selectivity of PBSC. Primary : tertiary selectivities of 1 : 14 and 1 : 24 have been obtained for photochlorination of 2,3-dimethylbutane in the presence of 4.0 M sulfur monochloride and 2.0 M phenyl sulfide.

Butane and isobutane were photochlorinated with molecular chlorine at 40° in the presence of 0.1 M n-butyl pentachlorophenyl sulfide. This concentration of sulfide was used because it approximately duplicated the concentrations of sulfide involved in the reactions of PBSC with butane and isobutane. The primary : secondary :

tertiary selectivity observed for these photochlorinations was

1 : 2.7 : 3.5.   This was identical, within experimental error, to

the value of 1 : 2.5 : 3.2 obtained for chlorination with molecular

chlorine alone.   Thus the presence of low concentrations of alkyl

pentachlorophenyl sulfides did not enhance the selectivity of chlorine

atoms.   In these photochlorination reactions in the presence of

added sulfide the yields of alkyl chlorides were in the order of 50-60%

of that expected from the amount of chlorine present.   Recovery of

the sulfide and analysis by nmr* showed that the sulfide itself had

undergone substantial chlorination, especially in the α-position.

Approximate values for the reactivity of n-butyl pentachlorophenyl

sulfide relative to the reactivity of butane and isobutane toward

chlorine atoms were 17 : 1 and 27 : 1 respectively (see the Appendix

for the method of calculating relative reactivities).

PBSC itself was tested as a possible complexing agent by

treating isobutane with approximately equimolar amounts of PBSC

and molecular chlorine.   Reaction conditions and analyses were the

same as used for the PBSC-isobutane reactions.   Product yields are

quoted in Table IV along with the selectivities calculated from these

yields.   The selectivity obtained for the PBSC-chlorine mixtures was

1 : 11, while that predicted, even if no complex formation occurred,

was 1 : 15.   Therefore, PBSC could also be eliminated as a complex-

ing agent.   The failure of PBSC and n-butyl pentachlorophenyl sulfide

to enhance the selectivity of chlorine atoms by complex formation

was understandable when the low concentrations (0.1 M) were taken

_____

* Abbreviation used for nuclear magnetic resonance.

TABLE IV

PRODUCT YIELDS IN THE PHOTOINITIATED REACTION OF ISO-
BUTANE WITH MIXTURES OF PBSC AND MOLECULAR CHLORINE
AT 40°.[a]

	mole/mole PBSC + Cl_2	
	Run 15[b]	Run 16[b]
iso-C_4H_9Cl	0.22	0.21
t-C_4H_9Cl	0.22	0.22
X	0.16	0.16
XI	0.23	0.22
C_6Cl_6	0.02	0.02
$(C_6Cl_5S)_2$	0.07	0.07
primary : tertiary selectivity	1 : 10.6	1 : 10.7

[a] Reaction mixtures contained 50 mmole of isobutane in 10 ml
of carbon tetrachloride and 1.00 mmole of Freon 112 as
internal standard.

[b] Run 15 was with 1.69 mmole (55 mole %) of PBSC and 1.37
mmole (45 mole %) of chlorine. Run 16 was with 1.60 mmole
(54 mole %) of PBSC and 1.37 mmole (46 mole %) of chlorine.

into account, since significant increases in selectivity usually
require much greater concentrations (2-12 M) of complexing agent
(16).

Bispentachlorophenyl disulfide was not examined as a possible
complexing agent due to the difficulties posed by its low solubility.
Also, it was presumed to react with chlorine since it was the probable
intermediate in the chlorinolysis of pentachlorothiophenol to give
PBSC.

$$2 \text{ ArSH} \xrightarrow{\text{Cl}_2} [\text{ArSSAr}] \xrightarrow{\text{Cl}_2} 2 \text{ ArSCl}$$

Having eliminated complexed chlorine atoms from consider-
ation, hydrogen abstraction by pentachlorophenylthiyl radicals was
considered next.

V.   REACTION OF BISPENTACHLOROPHENYL DISULFIDE (I)
      WITH CYCLOHEXANE AND ISOBUTANE.

Thiyl radicals have been generated by photolysis of disulfides
(22, 23, 24).   Pentachlorophenylthiyl radicals were generated by
photodissociation of I (log ϵ 2.22 at 400 mμ) promoted by irradiation
with an incandescent light source ($\lambda \geqslant$ 310 mμ using
Pyrex equipment).   Because of the low solubility of I
in hydrocarbon - carbon tetrachloride mixtures, reactions
were carried out at 80°.

Photolysis of I in cyclohexane-carbon tetrachloride gave
pentachlorothiophenol and cyclohexyl pentachlorophenyl sulfide in 5%

yield after 150 hr, in addition to recovered starting material.

$$\text{(cyclohexane)} + ArSSAr \xrightarrow[\text{CCl}_4,\ 80^\circ]{h\nu} ArSH \ + \ \text{(cyclohexyl-SAr)}$$

$$\begin{array}{ccc} & VI & III \\ & (5\%) & (5\%) \end{array}$$
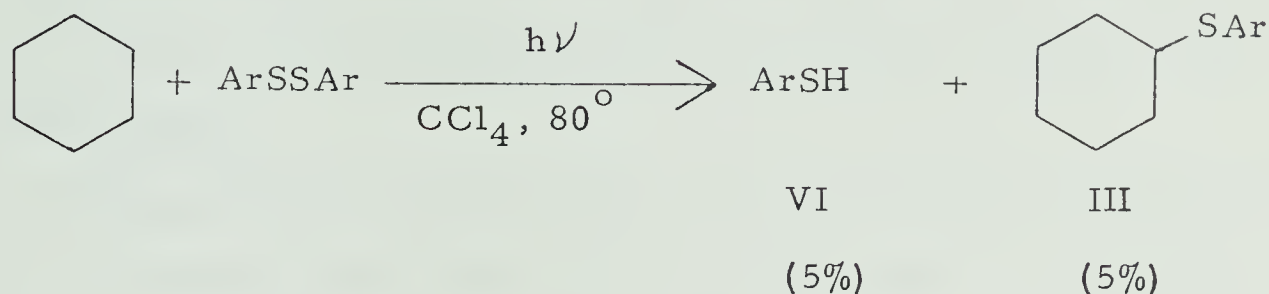
The reaction must have involved hydrogen abstraction by ArS·.

$$\text{(cyclohexane)} + ArS\cdot \longrightarrow ArSH \ + \ \text{(cyclohexyl·)}$$
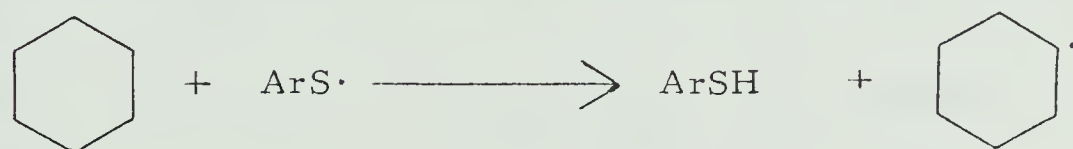
Under the reaction conditions used (long photolysis times) two reactions

explained the sulfide equally well.   The first reaction represented

$$\text{(cyclohexyl·)} + ArSSAr \longrightarrow \text{(cyclohexyl-SAr)} + ArS\cdot$$

$$\text{(cyclohexyl·)} + ArS\cdot \longrightarrow \text{(cyclohexyl-SAr)}$$
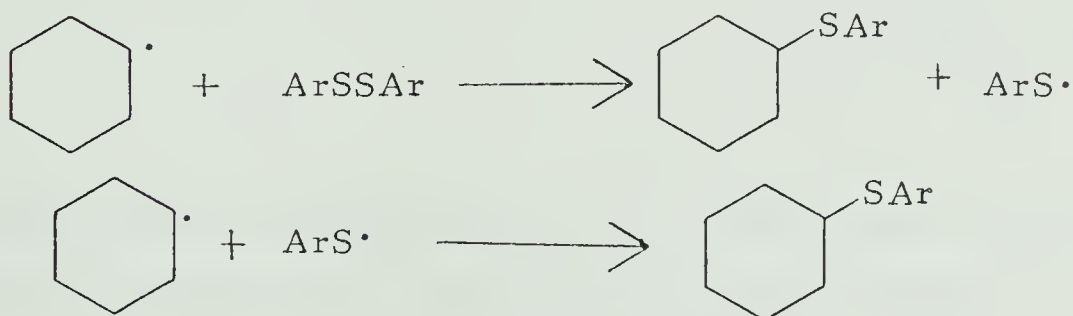
a chain reaction sequence and the second a nonchain sequence.

When I was treated with excess cyclohexane in carbon tetra-

chloride for two days at 80° using 10 mole % of benzoyl peroxide as

the initiator, VI and III were obtained in 2% yield and 18% yield

respectively.   Since the yield of III was about the maximum possible

yield assuming 100% efficiency for the initiator (10 mole % of I giving

two initiator radicals per mole of initiator) no definite conclusions

could be drawn regarding the chain or nonchain nature of the reaction.

Since VI was produced in the reaction, albeit in very low yield,

some hydrogen abstraction by pentachlorophenylthiyl radicals must

have taken place.

Using isobutane as substrate, the photoinitiated reaction went

nearly to completion after 50 hr of irradiation at 80°. In addition

to a small amount of recovered starting material, the reaction

yielded pentachlorothiophenol (80%), t-butyl pentachlorophenyl

sulfide (90%) and iso-butyl pentachlorophenyl sulfide (2-2.5%)

$$ArSSAr + (H_3C)_3CH \xrightarrow[CCl_4, \ 80^o]{h\nu} ArSH$$

$$VI$$

$$+ \ ArS - C(CH_3)_3$$

$$XI$$

$$+ \ ArS - CH_2 - CH(CH_3)_2$$

$$X$$
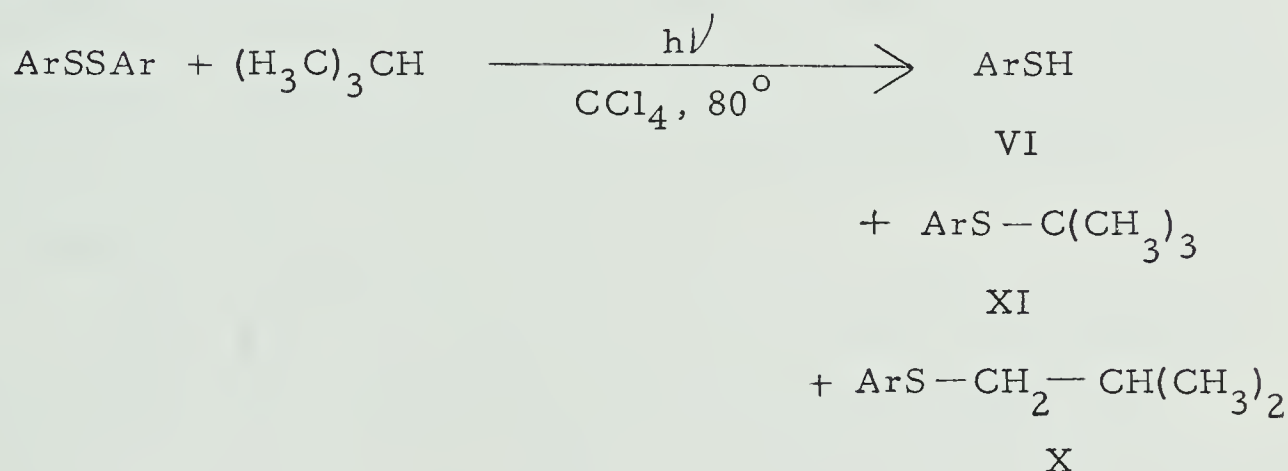
The ratio of XI to X estimated was 40 : 1 which gave a primary :

tertiary selectivity of 1 : 360 for pentachlorophenylthiyl. This

selectivity had to be considered as only an apparent selectivity

because of the strong possibility that the hydrogen abstraction step

was reversible (18). If this is the case, then the (apparent) select-

ivity should be dependent on the concentration of the thiophenol. The

reactions below illustrate how the thiophenol can influence the

selectivity by reversal of hydrogen abstraction.

(primary)   R· + ArSH ⟶ (primary) RH + ArS·

(tertiary)   RH + ArS· ⟶ (tertiary) R· + ArSH

These two reactions when summed provide a means whereby a primary alkyl radical exchanges with a tertiary alkyl hydrogen to give a tertiary alkyl radical and a hydrocarbon molecule in the presence of pentachlorothiophenol. Further work is required to enable a fuller understanding of this aspect of the present work. Two experiments which can be suggested are first to carry out the photolytic reaction in the presence of added pentachlorothiophenol, and second to repeat the photolytic reaction using deuterium labelled isobutane (tertiary hydrogen) and to analyze the products for scrambling of hydrogen and deuterium.

When I was reacted with isobutane in carbon tetrachloride for two days at $80°$ using 10 mole % of benzoyl peroxide as the initiator, the yield of VI was 24%, of XI 34% and of X about 2%. The moderate yield of products obtained in this benzoyl peroxide initiated reaction required a short chain reaction. The mechanism below was considered to explain best the results obtained above.

$$(In)_2 \xrightarrow{\Delta} 2\ In·$$

$$In· + RH \longrightarrow R· + InH$$

$$R· + ArSSAr \longrightarrow \underline{ArSR} + ArS·$$

$$ArS· + RH \longrightarrow \underline{ArSH} + R·$$

$$2\ ArS· \longrightarrow ArSSAr$$

$$(In)_2 = (C_6H_5-\overset{O}{\overset{\|}{C}}-O-)_2$$
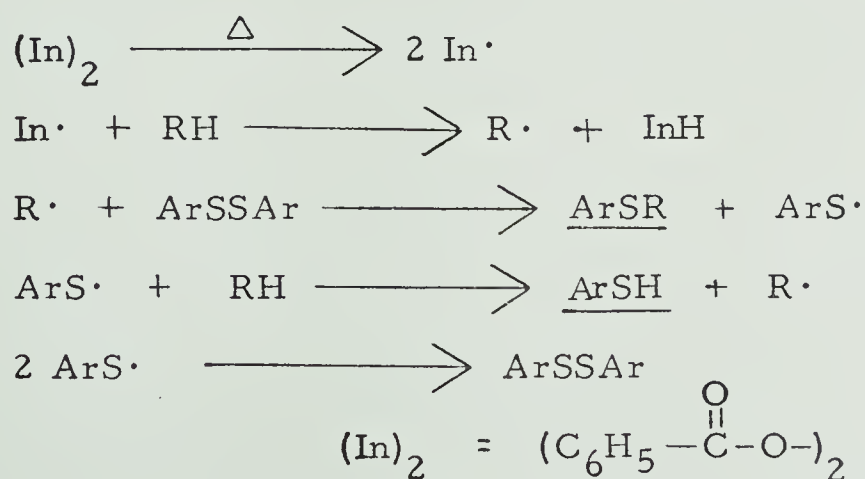
Since the yield of VI was less than that of XI some of the thiophenol may have disappeared by hydrogen donation to initiator radicals,

$$ArSH \ + \ In\cdot \ \longrightarrow \ ArS\cdot \ + \ InH$$
$$2 \ ArS\cdot \ \longrightarrow \ ArSSAr$$
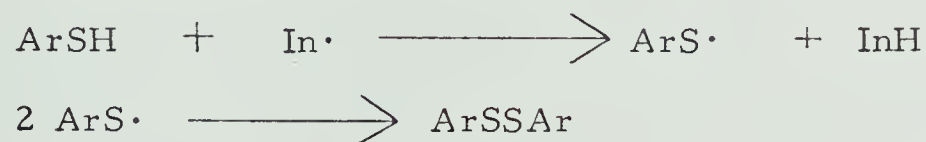
or by reversal of the hydrogen abstraction reaction.

Cyclohexane was less reactive than isobutane in both the photoinitiated and benzoyl peroxide initiated reactions, an observation which might have been expected because the secondary hydrogens of cyclohexane should be much less reactive than the tertiary hydrogen of isobutane toward a very selective (stable) radical such as pentachlorophenylthiyl.

Perhaps the most significant inference to be made from the results of the benzoyl peroxide initiated reaction of I with isobutane was that the displacement reaction by alkyl radicals on the S-S bond of I was a feasible reaction and could therefore be included with justification in the reaction schemes (Scheme I-IV), for the photoinitiated substitution reactions of PBSC.

DISCUSSION

The reaction schemes outlined in the Introduction of this section are based on selectivities. In addition, Scheme I could be tested by finding out if PBSC reacted with hydrogen chloride. Since it did not, Scheme I was considered an untenable mechanism. As well, this scheme predicted a short chain reaction because the only fate of the pentachlorophenylthiyl radicals (ArS·) was the coupling reaction.

$$2 ArS \cdot \longrightarrow ArSSAr$$

In view of the moderate chain lengths observed (40-100), Scheme I was even less likely as a possible mechanism.

Scheme II predicted a selectivity similar to chlorine atoms, Scheme III predicted a selectivity similar to ArS·, and Scheme IV predicted a selectivity intermediate between chlorine atoms and ArS·. Because the primary : tertiary selectivity with isobutane at 40° observed for PBSC (1 : 25) was intermediate between that of chlorine atoms (1 : 3.2) and ArS· (1 : 360), Scheme IV best explained free-radical substitution reactions of PBSC. However, minor contributions from Schemes II and III could not be eliminated on the basis of selectivities.

For cyclohexane which was less reactive than isobutane toward ArS·, and for which selectivities could not be used as a criterion for evaluating the reaction schemes, Scheme II would be expected to play a more important role because it included an alternative reaction for

ArS·.

$$ArS· + ArSCl \longrightarrow ArSSAr + Cl·$$

Other observations must be taken into account when considering the reaction schemes. The first of these is that alkyl pentachlorophenyl sulfides exhibited a high reactivity relative to hydrocarbons toward chlorine atoms. This was observed in the photochlorination with molecular chlorine of butane and isobutane in the presence of added n-butyl pentachlorophenyl sulfide. The high relative reactivity of the sulfide (20-30 relative to the hydrocarbons) means that significant chlorination of the sulfides should have occurred during the course of reaction of PBSC with hydrocarbons. However, this was not observed. A tentative explanation for this is as follows. In the early stages of the PBSC-hydrocarbon reactions the concentrations of the sulfides would be low so they could not compete with the hydrocarbon molecules for reaction with chlorine atoms. As the concentration of the sulfides increased so did the concentration of the other products including bispentachlorophenyl disulfide. If the chlorine atoms reacted with the disulfide, then fewer chlorine atoms would be available for hydrogen abstraction from hydrocarbon or the sulfides.

$$Cl· + ArSSAr \longrightarrow ArSCl + ArS·$$

Two important consequences of such an explanation are that the reaction chain length and the selectivity should vary with the extent

of reaction. The chain length should decrease and the selectivity should increase in the later stages of reaction as the above reaction comes into play, thus increasing the concentration of ArS· and decreasing the concentration of chlorine atoms. Further work is required to settle this point.
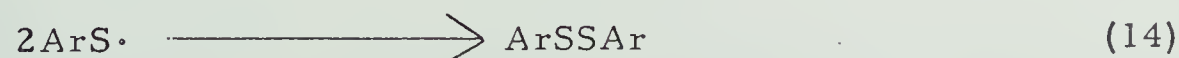
Proposal of ArS· as a hydrogen abstracting radical required that pentachlorothiophenol (ArSH) was a reaction intermediate or product. The product analyses (runs 5, 12 and 14) showed that the final concentration of ArSH in the reaction mixtures was 10^{-3} M or less. Kharasch and Ariyan (11) proposed an ionic reaction between ArSH and PBSC (equation 5) to account for the disappearance of ArSH. This was checked in the following way. To two cyclohexane reaction mixtures (runs 8 and 9) was added some ArSH (15 mole % of PBSC). In these reactions precipitation of bispentachlorophenyl disulfide began earlier than in the reactions run without added ArSH (10-15 minutes as compared with one hour or more). Analysis of the completed reactions showed that the final concentration of ArSH was the same in both cases. From this the conclusion could be drawn that the ionic reaction (equation 5) was fast enough to account for the low final concentrations of ArSH in the reaction mixtures. In addition, it was likely that the concentration of ArSH never became very large (relative to reactants and products) during the course of the reactions, and as a consequence the reversal of hydrogen abstraction

$$\text{ArSH} + \text{R·} \longrightarrow \text{ArS·} + \text{RH}$$

would be expected to not have been too important.

On the basis of the results of this study, the following
mechanism which is a combination of Schemes II, III and IV originally
considered, can be proposed as a general description of the free-
radical substitution reactions of PBSC with saturated hydrocarbons.
Sufficient information was not obtained to assess fully the relative
importance of some of the reactions. The relative contribution of
hydrogen abstraction by chlorine atoms (equation 7) and by ArS·
(equation 8) is expected to vary with the hydrocarbon substrate under
consideration. The termination reaction shown (equation 14) was
considered the most likely termination step because the high select-
ivity of ArS· implies a relatively high stability for this radical and
therefore coupling should be a favorable reaction for it to undergo.

$$ArSCl \xrightarrow{h\nu} ArS\cdot + Cl\cdot \qquad (6)$$

$$Cl\cdot + RH \longrightarrow HCl + R\cdot \qquad (7)$$

$$ArS\cdot + RH \rightleftharpoons ArSH + R\cdot \qquad (8)$$

$$R\cdot + ArSCl \longrightarrow RCl + ArS\cdot \qquad (9)$$

$$R\cdot + ArSCl \longrightarrow ArSR + Cl\cdot \qquad (10)$$

$$R\cdot + ArSSAr \longrightarrow ArSR + ArS\cdot \qquad (11)$$

$$ArS\cdot + ArSCl \rightleftharpoons ArSSAr + Cl\cdot \qquad (12)$$

$$ArSH + ArSCl \longrightarrow ArSSAr + HCl \qquad (13)$$

$$2ArS\cdot \longrightarrow ArSSAr \qquad (14)$$
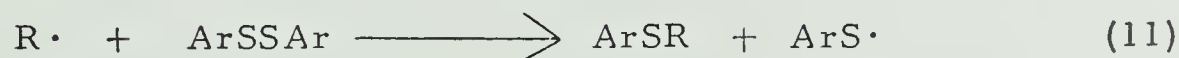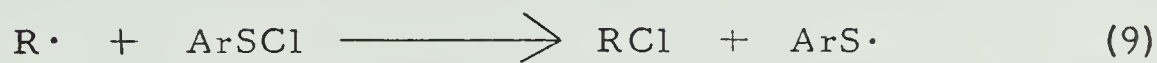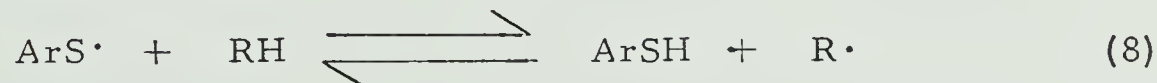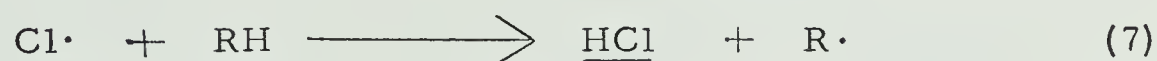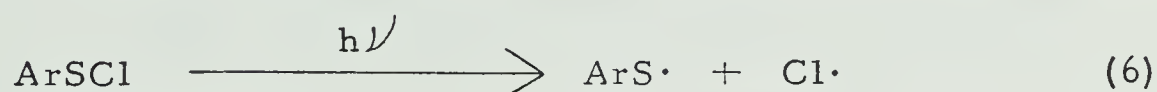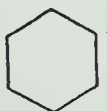
The quantitative results of this study could be used to compare PBSC to other sulfenyl chlorides. The steric effect observed by Harris (13) in displacement reactions of alkyl radicals on trifluoromethanesulfenyl chloride (TFMSC) was also evident with PBSC. To illustrate this effect it was best to define the ratio of the yield of alkyl pentachlorophenyl sulfide to the yield of alkyl chloride (ArSR/RCl) as a given quantity, the S value. This quantity was an approximate measure of the ratio of displacement on sulfur to displacement on chlorine. The S values for PBSC and trifluoromethanesulfenyl chloride are compared in Table V.

TABLE V

S VALUES FOR VARIOUS ALKYL RADICALS WITH PBSC AND

TRIFLUOROMETHANESULFENYL CHLORIDE.

Radical	S Value[a]	
	PBSC[b]	TFMSC[c]
$CH_3CH_2CH_2CH_2\cdot$	40	13
$H_3C - \underset{\underset{H}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}} - CH_2\cdot$	19	12
$CH_3CH_2\dot{C}HCH_3$	5.6	3.8
⬡	3.5	1.6
$CH_3 - \underset{\underset{\bullet}{\vert}}{\overset{\overset{CH_3}{\vert}}{C}} - CH_3$	2.5	0.7

[a] Defined in text.   [b] At 40°.   [c] Taken from reference 13.

As can be seen from this table a close parallel exists between
the two sulfenyl chlorides in this regard. Harris has interpreted
this effect in terms of the ease of approach of R· to the sulfur atom
of the sulfenyl chloride; trichloromethanesulfenyl chloride gave
only alkyl chlorides (8) because the trichloromethyl group effectively
blocked the approach of R· to the sulfur atom (13). The substitution
reactions of sulfenyl chlorides appear to fall into two categories.
The first, exemplefied by PBSC and TFMSC, involves a mixed chain
where thiyl radicals and chlorine atoms both abstract hydrogen and
where displacement occurs both on sulfur and chlorine to give sulfides
and chlorides. The second, exemplefied by TCMSC, is less complex;
displacement occurs only on chlorine and therefore hydrogen abstract-
ion is by thiyl radicals only.

Inclusion of this concept of steric effect into the discussion
now allows consideration of an observation which merits discussion
at greater length.

Reaction of isobutane with mixtures of chlorine and PBSC
(runs 15 and 16) gave a selectivity of 1 : 11 while that predicted was
1 : 15. Since hydrogen abstraction by chlorine atoms must have given
a large proportion of primary radicals, some of these radicals must
have undergone chain transfer with PBSC (in competition with Cl_2) to
give a large proportion of displacement on sulfur thus freeing more
chlorine atoms for hydrogen abstraction. The result was a selectivity
actually lower than that predicted for the same mixtures of chlorine
and PBSC reacting independently, and this result could now easily be

explained by a mixing of the two reactions.

In closing, some mention must be made of the one side reaction observed. Hexachlorobenzene was observed as a minor reaction product (1-4% based on PBSC) in all of the reactions run with PBSC. One explanation considered for this was a displacement reaction analagous to that observed by Miller and Walling for displacement of bromine atoms from bromobenzene by chlorine atoms (39), and by Tanner and Van Bostelen for displacement of iodine from iodobenzene by chlorine atoms (40). The yield of hexachlorobenzene did not increase in the reactions using mixtures of chlorine and PBSC thus discounting the feasibility of proposing a displacement reaction on PBSC by chlorine atoms. A precedent for obtaining hexachloro-benzene as a product during free-radical reactions of PBSC was that thermolysis of benzenesulfenyl chloride gave chlorobenzene (60%) plus diphenyl disulfide and sulfur monochloride (41).

Because photolysis of PBSC was reported to give bispenta-chlorophenyl disulfide (42), a sample of PBSC was photolyzed under our reaction conditions. After photolysis for 24 hr 68% of the active halogen remained both as volatile and nonvolatile products. Also, a 17% yield of hexachlorobenzene was isolated from the reaction mixture. This experiment did not shed any light on the mechanism by which hexachlorobenzene arose, but it did show that hexachloro-benzene was one of the products of photolysis of PBSC. The follow-ing reactions might be an explanation of how this product arises from photolysis of PBSC in carbon tetrachloride:

$$\text{ArSCl} \xrightarrow{\quad h\nu \quad} \text{ArS·} + \text{Cl·}$$

$$\text{ArS·} \xrightarrow{\hspace{3cm}} \text{Ar·} + \text{S}$$

$$\text{Ar·} + \text{ArSCl} \xrightarrow{\hspace{2cm}} \text{ArCl} + \text{ArS·}$$
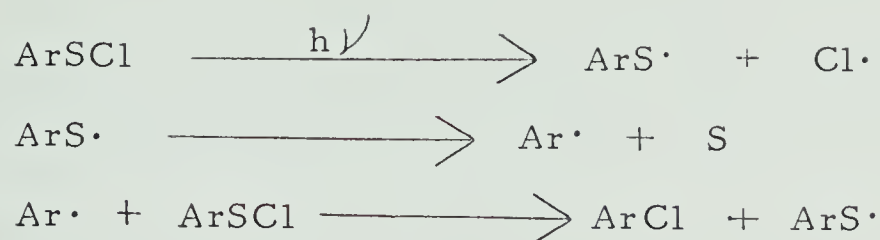
Although speculative, this proposal seemed to present a plausible pathway by which hexachlorobenzene could appear as a product of the photolysis of PBSC.

SUMMARY

A good material balance was obtained for the photoinitiated substitution reaction of PBSC with cyclohexane. A chain length of 40-100 was estimated for the reaction with cyclohexane by initiation with a few mole % of AIBN. The primary : secondary : tertiary selectivity found for PBSC was 1 : 8 : 25 using butane and isobutane as substrates. A mixed chain with chlorine atoms and pentachloro-phenylthiyl radicals as chain carrying radicals was proposed to account for this selectivity.

The photoinitiated and benzoyl peroxide initiated reactions of bispentachlorophenyl disulfide with isobutane and cyclohexane were studied. It was found that the pentachlorophenylthiyl radical can readily abstract a tertiary hydrogen atom from isobutane. In benzoyl peroxide initiated reactions carried out under identical conditions, cyclohexane was found to be less reactive than isobutane as shown by a lower yield of products. The results of these benzoyl peroxide initiated reactions also allowed the inclusion into the reaction

mechanism of a displacement reaction on the disulfide by alkyl radicals. This reaction has not been included in previous reaction mechanisms proposed for substitution reactions of sulfenyl chlorides (8, 11, 13).

A steric effect was observed for displacement reactions on the sulfenyl chloride by alkyl radicals. This steric effect was similar to that previously observed for trifluoromethanesulfenyl chloride (13).

Hexachlorobenzene was a minor reaction product. Photolysis of PBSC in the absence of hydrocarbon substrates gave hexachloro-benzene (17% yield). Photolytic cleavage of the aryl sulfur bond was put forth as a tentative explanation for the occurrence of hexachlorobenzene as a product arising from the photolysis of PBSC in carbon tetrachloride.

EXPERIMENTAL

I. MATERIALS

Pentachlorothiophenol (Aldrich Chemical Co., technical grade) was purified by crystallization from benzene-carbon tetrachloride (2 : 1 v/v). It had m.p. 238-240° (sealed tube). Chlorine (Matheson) was dried by passing through concentrated sulfuric acid.

For crystallization, Shawinigan reagent grade carbon tetrachloride, benzene and acetone were used. For analytical work Fisher Spectranalyzed reagent grade carbon tetrachloride was used; purified benzene was prepared for analytical work by twice crystallizing reagent grade material and was free from impurities by glpc and nmr.

Cyclohexane was Phillips pure grade or research grade; butane and isobutane were Phillips research grade gases.

Freon 112 (1,1-difluoro-1,2,2,2-tetrachloroethane) was distilled through a three foot helices packed column and had b.p. 89.5-90.0^o (700 mm). No impurities were detected by glpc. Hexachlorobenzene was Eastman practical grade material recrystallized once from benzene, m.p. 228-229° (sealed tube).

Azobisisobutyronitrile (AIBN) was purified by one recrystallization from methanol and dried over phosphorus pentoxide. Benzoyl peroxide (Fisher Scientific) was used as supplied.

II.   METHODS AND PROCEDURES

GENERAL PROCEDURE FOR REACTIONS

Reaction ampoules were made of Pyrex tubes joined to 10/30 joints, the total volume being about twice that of the reactant solution used. The ampoules were cleaned with chromic acid solution, distilled water, concentrated ammonium hydroxide and distilled water, then oven-dried at 110°. In subdued light, the reactants, solvent and standard were placed in the ampoules which were then degassed by one cycle of freeze-thaw at ca. 10^{-5} mm. After degassing was completed, the ampoules were sealed under vacuum, let warm, and then equilibrated at the desired temperature (40°, 71° or 80°) in a Pyrex water bath. The usual light source for irradiation was two 200 w incandescent lamps placed at a distance of three to four inches from the ampoules. Ampoules were kept in the dark by wrapping in aluminum foil.

Removal of solvent or evaporation of solvent refers to the removal of the solvent (and other volatile components) on a rotary evaporator using water aspirator vacuum and a water bath at $30-70^\circ$.

GAS LIQUID PARTITION CHROMATOGRAPHY (glpc)

For glpc analyses two instruments were used. The instruments and columns are described below. All of the columns were constructed of stainless steel.

1. Varian Aerograph model 202 with thermal conductivity detector and linear temperature programmer. Two columns were used:

a) 10' by 1/4" SF-96, 10% on 60/80 Firebrick

b) 5' by 1/4" SE-30, 15% on 60/80 Chromsorb W.

2. Varian Aerograph model 600-D with flame ionization detector.
Four columns were used:

a) 20' by 1/8" SF-96, 5% on 80/100 Chromsorb W, AW-DMCS

b) 25' by 1/8" UCON POLAR, 5% on 80/100 Chromsorb W

c) 5' by 1/8" SE-30, 5% on 60/80 Chromsorb W

d) 5' by 1/8" QF-1, 5% on 100/120 Chromsorb W.

Analyses were carried out in triplicate. Peak areas were measured by multiplying peak height times peak width at one-half peak height. Calibration curves were used to convert the area ratios of the alkyl chlorides (relative to Freon 112 as internal standard) into molar ratios. Precision of glpc analyses was generally 1-3%. Where quoted, the experimental uncertainties are standard deviations from the mean. Retention time comparison and peak enhancement refer to addition of authentic material to a portion of the sample and reanalysis by glpc.

SPECTRAL MEASUREMENTS

Infrared (IR) spectra were recorded on a Perkin Elmer model 421 recording spectrophotometer. Ultraviolet-visible spectra were recorded on a Perkin Elmer model 202 recording spectrophotometer. The nmr spectra are proton spectra. Chemical shifts are expressed in τ units and are relative to tetramethylsilane (TMS, $\tau = 10.000$). The spectra were obtained on a Varian Associates A-60 or A-56/60A

high resolution nmr spectrometer. Mass spectra were obtained on Metropolitan Vickers MS2 or Associated Electronics Ltd., MS9 machines using an ionizing voltage of 70 ev.

PHYSICAL CONSTANTS

All melting points and boiling points are uncorrected. Melting points were obtained with a Fisher-Johns melting point apparatus, except for sealed tube melting points for which a Mel-Temp apparatus (Laboratory Devices) was used. Refractive indices were measured on a Bausch and Lomb refractometer.

MICROANALYSES

Microanalyses were performed in the microanalytical laboratory, Chemistry Department, University of Alberta, Edmonton.

III. PENTACHLOROBENZENESULFENYL CHLORIDE (PBSC)

The method of Putnam and Sharkey (38) was used to prepare PBSC by the reaction of molecular chlorine with pentachlorothiophenol. Their method was modified by allowing the reaction mixture to stand overnight after reflux was stopped. Removal of the solvent gave material of high purity which could be used without further purification. The reaction and isolation of product were carried out in subdued light.

Pentachlorothiophenol (10 g, 0.035 mole), iodine (0.1 g) and dry carbon tetrachloride (200 ml) were placed in a three-neck flask equipped with gas inlet and reflux condenser. For 5 hr the solution

was heated to reflux while chlorine was bubbled through. At first

a deep red color developed which turned to orange after 1-2 hr.

The reaction mixture was cooled to ambient, saturated with chlorine

and let stand overnight. Excess chlorine was removed by distilling

at a water aspirator for 10-15 minutes, then the solvent was removed

on a rotary evaporator. The yield of orange solid was 11.3 g (101%),

m.p. 103-104°.

Anal. Calculated for C_6Cl_6S: Cl, 67.14. Found: Cl, 67.55.

The material was stored at room temperature protected from

light and atmospheric moisture.

The following iodometric titration procedure was used to

determine the purity of the material. The sulfenyl chloride was

weighed into a flask and dissolved in 25 ml of carbon tetrachloride.

A magnetic stirring bar, 2 g of potassium iodide and 25 ml of 10%

aqueous acetic acid were added. The flask was stoppered and the

contents stirred for 0.5 hr. The liberated iodine was titrated with

standard sodium thiosulfate solution. A 1 : 1 molar stoichiometry

was used for calculating the theoretical titer.

$$2\ C_6Cl_5SCl\ +\ 2\ KI\ \longrightarrow\ C_6Cl_5SSC_6Cl_5\ +\ I_2\ +\ 2\ KCl$$

$$2\ S_2O_3^=\ +\ I_2\ \longrightarrow\ S_4O_6^=\ +\ 2\ I^-$$
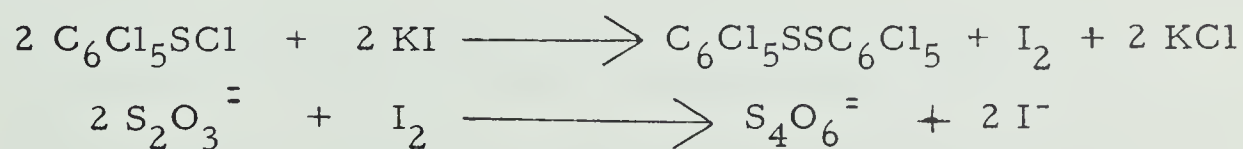
PBSC, g	ml 0.1000 M $Na_2S_2O_3$	
	found	required
0.3788	11.80	11.95
0.3661	11.49	11.55

% purity = 99.1 $\pm$ 0.4

Soon after mixing of reagents, a solid precipitated. It was collected by filtration and identified as bispentachlorophenyl disulfide by its melting point of 234-236°. Lit. (11) m.p. 235-236°. After filtering off the solid, the carbon tetrachloride solution was concentrated and examined by glpc (model 600-D, 5' SE-30 at 200°, 15 psi N_2). A small amount of hexachlorobenzene was found by comparison of retention time with authentic material.

Other batches of PBSC had purities of 99-100% by iodometric titration when freshly prepared. Material a few weeks old had titrimetric purities of 97-98%.

IV.   BISPENTACHLOROPHENYL DISULFIDE (I)

PBSC(1.90 g, 6.0 mmole), pentachlorothiophenol (1.75 g, 6.1 mmole) and 25 ml of dry carbon tetrachloride were heated to reflux for 0.25 hr. The solvent was evaporated and the crude product crystallized from benzene. The yield of orange crystals was 1.75 g (53%), m.p. 235.5-237°. Mixture m.p. with the material isolated from the iodometric titration was 235-237°.

V.   REACTION OF PBSC WITH CYCLOHEXANE (RUNS 1-10)

Between 0.47 and 0.50 g of PBSC (1.48-1.56 mmole) was weighed accurately into an ampoule. Then 3.00 ml of carbon tetrachloride was pipeted in (0.200 M in Freon 112 for runs 3-10), followed by 2.00 ml of cyclohexane (pure grade). Runs 8 and 9 contained 0.060 g (0.21 mmole) of pentachlorothiophenol. The ampoules were

degassed in the dark by one cycle of freeze-thaw, sealed under vacuum, wrapped in aluminum foil and equilibrated at the desired temperature. The foil was then removed and irradiation begun. At first the reaction mixtures were orange-colored. After about one hr the color had faded to a light yellow and orange solid (I) began to crystallize out (except for the 80° runs). After 5-10 hr, the reaction mixtures were colorless and crystallization of the solid had apparently been completed. In the reactions containing added pentachlorothiophenol, solid began to crystallize out after 10-15 minutes.

Hydrogen chloride was identified by bubbling the escaping gas from a freshly opened ampoule through water. On separate portions, a positive test for chloride ion was obtained with silver nitrate, and addition of potassium iodide and potassium iodate caused liberation of iodine. For determination of hydrogen chloride the ampoules were frozen in liquid nitrogen and broken open under 50-100 ml of water in a stoppered flask. The flask was shaken for 10-15 minutes. The hydrogen chloride was titrated as iodine liberated after addition of 1 g of potassium iodate and 2 g of potassium iodide (43).

$$6 H^{+} + 5 KI + KIO_3 \longrightarrow 3 H_2O + 6 K^{+} + 3 I_2$$

$$2 S_2O_3^{=} + I_2 \longrightarrow S_4O_6^{=} + 2 I^{-}$$
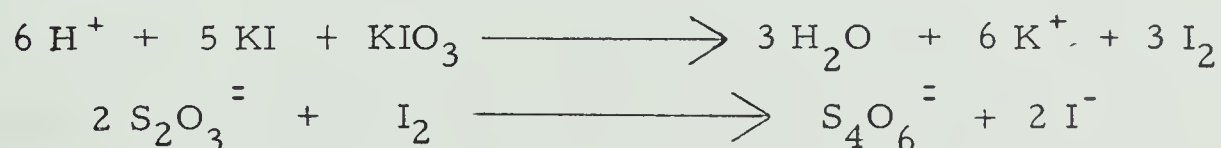
For determination of organic products, the reaction products were first analyzed by glpc for cyclohexyl chloride (II) (model 202, 10' SF-96 column at $75-150^{\circ}$, 40 ml He/min), and identified by comparison of retention time with authentic material. The qualitative

product study was done on runs 3, 4, 5, 6 and 8.

After glpc analysis of run 4, precipitated solid was collected, dried and weighed. Yield of orange crystals was 0.157 g, m.p. 235-237°; mixture m.p. with I 234-236°. Evaporation of the filtrate gave 0.353 g of white solid m.p. 109.5 – 112°. Analysis by glpc (model 202, 5' SE-30 at 240°, 60 ml He/min) showed two components in the ratio 3 : 97 by area. The first was identical to hexachloro-benzene (IV) in retention time, and the mass spectrum of a collected sample was identical to the mass spectrum of an authentic sample of hexachlorobenzene (parent ions at m/e 282, 284, 286 and 288 were present with the intensities expected for a molecule containing six chlorine atoms, and were the most intense peaks in the spectrum). The mass spectrum of the crude sulfide had a set of parent peaks at m/e 362, 364, 366, 368 and 370 ($C_6{}^{35}Cl_5SC_6H_{11}$ = 362). The relative intensities were those expected for a molecule containing five chlorine atoms. A small set of parent peaks (2-3% of parent peaks for $C_6Cl_5SC_6H_{11}$) appeared at m/e 394, 396, 398, 400, 402 and 404. It appeared to be from $C_6Cl_5SC_6H_{10}Cl$ and $C_6Cl_5SC_6H_{11}S$ as fragments were present with approximately equal intensities at m/e 117 and 119 ($C_6H_{10}{}^{35}Cl$ and $C_6H_{10}{}^{37}Cl$), and at m/e 115 ($C_6H_{11}S$). A similar mass spectrum was obtained for the crude sulfide from run 6 (m.p. 110-113°).

Thin-layer chromatography (CS_2) of the sulfide from run 3 showed a trace amount of a material moving just ahead of the main compound and possessing the same R_f as I. Treatment of the sulfide

with acetone left 0.01 g of insoluble I m.p. 230-235°. Crystallization

of the soluble portion gave 0.222 g of white needles m.p. 115-116°,

lit. (11) m.p. 116° for cyclohexyl pentachlorophenyl sulfide (III);

nmr (CCl$_4$) τ 6.4-7.0 (m, 1, ArS $-$ C $-$H), τ 7.8-9.0 (m, 10, ring

protons); IR (CS$_2$) 2935, 2855 (C-H), 1331, 1327, 1309, 1303

(aromatic C $=$ C) and 687 cm^{-1} (C-Cl).

One reaction (run 10) was carried to partial completion.

After 0.5 hr of irradiation, the color of the reaction mixture had

changed from orange to yellow and crystals of I were just beginning

to form. The contents of the ampoule were stirred with potassium

iodide-aqueous acetic acid. Titration of the iodine liberated

showed that 25% of the PBSC remained.

A small aliquot of the organic layer was removed for glpc

analysis for cyclohexyl chloride.

The organic layer was separated, washed once with water and

dried by passing through a small pad of silica gel. Removal of the

solvent gave the crude sulfide. A yellow contaminant (presumably I)

was removed by two operations of treating with a few ml of carbon

tetrachloride, filtering to remove insoluble yellow matter and

evaporation of the filtrate. The yield was 0.255 g, m.p. 112-114°.

Analysis by glpc showed only III and IV in the ratio 98 : 2.

Analysis for traces of pentachlorothiophenol could not be done

by glpc with the column used for analyzing the crude sulfide because

analysis required relatively large amounts (about 50 μg) before it

could be detected due to permanent retention of material. Several

other columns were tried unsuccessfully. Acetylation of the crude

sulfide mixture and analysis for traces of pentachlorophenyl thiol-

acetate (VII) proved to be a successful method of analyzing for traces

of pentachlorothiophenol. Analysis of an equimolar mixture of hexa-

chlorobenzene and VII over a range of sample sizes of 10-30 μg of each

gave a constant peak area ratio (IV/VII) equal to 1.14. This independ-

ence of response from sample size proved that the thiolacetate unlike

the thiophenol was not permanently retained on the glpc column.

The following procedure was used to analyze the crude sulfide

from run 8 for traces of pentachlorothiophenol.

The sulfide (0.100 g) and excess acetyl chloride (0.5 ml) were

heated to reflux in 5 ml of carbon tetrachloride. Pyridine (0.5 ml)

in 5 ml of carbon tetrachloride was added in small portions through

the reflux condenser. After 0.5 hr the reaction mixture was cooled

and poured onto ice. The carbon tetrachloride layer was separated

and washed with ice-cold 3 N hydrochloric acid (2 x 30 ml). After

drying over anhydrous calcium chloride the solvent was removed to

give 0.094 g of material (94% recovery). Analysis by glpc (model

202, 5' SE-30 at 230°, 60 ml He/min) showed the appearance of a

component possessing the same retention time as VII, amounting to

about 0.2% of the products in the trace, or less than 0.2% based on

PBSC.

A further 0.100 g of sulfide from run 8, to which was added

0.2 mg of VI, was acetylated by the same procedure. Analysis by

glpc showed that the peak for the thiolacetate (VII) had doubled in size.

This illustrated that the acetylation technique was sufficiently

quantitative and sensitive to be a valid means of analyzing for traces

of pentachlorothiophenol.

Run 5 was analyzed by the same method. The amount of

pentachlorothiophenol detected (as the acetate) was 0.2% based on

PBSC.

VI.   PENTACHLOROPHENYL THIOLACETATE (VII)

Pentachlorothiophenol (0.28 g, 1.0 mmole) was acetylated

by the procedure above using the same quantities of reagents. There

was obtained 0.30 g (94%) of a pale yellow solid m.p. 116-118°, lit.

(44) m.p. 118-119°; IR (CS$_2$) 1722, 1708 (thiolester carbonyl) and

690 cm^{-1} (C-Cl).

VII.   SYNTHESIS OF THE ISOMERIC BUTYL PENTACHLORO-
       PHENYL SULFIDES, VIII-XI.

The sulfides were prepared by alkylating the sodium salt of

pentachlorothiophenol with the appropriate alkyl halide in boiling

ethanol (25 ml, 1 hr). Compounds VIII-X were isolated by pouring

the reaction mixtures onto 100 g of ice. VIII and X were collected

as solids which were crystallized from acetone-ethanol; m.p. of

VIII was 38°, lit. (45) m.p. 39-40° from methanol-ethanol.

Compound IX was obtained as a colorless oil which was extracted

into benzene. To obtain the t-butyl isomer (XI) free from starting

material, the solvent was evaporated and the residue treated with

excess 5% sodium hydroxide. The solid remaining was filtered off and crystallized from acetone-ethanol. Analytical samples of X and XI were prepared by sublimation at 110-120° (0.01 mm); m.p. of X was 37.5-38°, m.p. of XI was 122.5-123°. The entire crude yield of IX was distilled b.p. 135-145° (0.01 mm), n_D^{20} 1.6124. The analysis was obtained on this material. Table VI summarizes the details.

The IR spectra (CS_2) of all four isomers contained bands for C-H stretching between 2860 and 2980 cm^{-1}. The aromatic $C \rightleftharpoons C$ stretching appeared as two strong bands (split in VIII and X) at 1300-1305 cm^{-1} and at 1325-1335 cm^{-1}. The C-Cl stretching bands for all four isomers was a strong band between 683 and 686 cm^{-1}.

The nmr data of the four isomers are shown in Table VII.

VIII. REACTION OF PBSC WITH NORMAL BUTANE (RUNS 11 AND 12) AND ISOBUTANE (RUNS 13 AND 14)

PROCEDURE

The reaction mixtures consisted of ca. 3 mmole of PBSC (0.95-1.0 g), ca. 50 mmole of hydrocarbon (5 ml at -80°), 2.00 mmole of Freon 112 and 10 ml of carbon tetrachloride.

The reaction mixtures were degassed and irradiated at 40° in the same way as the cyclohexane reactions (runs 1-10). Irradiation times of 7-10 hr were required for complete reaction as shown by complete disappearance of the orange color of PBSC, and crystallization of the disulfide.

TABLE VI

THE ISOMERIC BUTYL PENTACHLOROPHENYL SULFIDES VIII-XI.

	mmole C_6Cl_5SH	mmole NaOH	alkylating agent (mmole)	yield %	Analysis C	H	Cl
VIII	10	12	n-C_4H_9Br (20)	80	-	-	-
IX	10	20	sec-C_4H_9Br (20)	83	35.54	2.61	52.17
X	10	12	iso-C_4H_9Br (20)	60	35.45	2.79	52.36
XI	10	20	t-C_4H_9Cl (20)	9	35.83	2.87	52.57
			Calcd. for $C_{10}H_9Cl_5S$:		35.48	2.70	52.37

56

TABLE VII

NUCLEAR MAGNETIC RESONANCE DATA OF THE ISOMERIC

BUTYL PENTACHLOROPHENYL SULFIDES (CCl_4).

	group assignment	τ value (multiplicity[a], J cps)
VIII	ArS-CH_2-[b]	7.12 (t, 6.5)
	-CH_2-CH_2-	8.5 (m, -)
	-CH_3	9.1 (m, -)
IX	ArS-$\overset{\mid}{\underset{\mid}{C}}$-H	6.66 (m, -)
	-CH_2-	8.45 (m, -)
	ArS-$\overset{\mid}{\underset{\mid}{C}}$-$CH_3$	8.77 (d, 6.5)
	-CH_3	8.97 (t, 7)
X	ArS-CH_2-	7.26 (d, 6.5)
	-C-H	8.32 (m, -)
	$H_3C-\overset{CH_3}{\underset{\mid}{\overset{\mid}{C}}}-$	8.99 (d, 6)
XI	ArS-$\overset{CH_3}{\underset{CH_3}{\overset{\mid}{\underset{\mid}{C}}}}$-$CH_3$	8.61 (s, -)

[a] s, singlet; d, doublet; t, triplet; m, multiplet.

[b] Ar= C_6Cl_5 group.

ANALYSIS AND IDENTIFICATION OF PRODUCTS

The ampoules were frozen in liquid nitrogen, broken open and analyzed for alkyl chlorides by glpc (model 600-D, 20' SF-96 at 50°, 15 psi N_2). The chlorides were identified by peak enhancement on two columns (20' SF-96 and 25' UCON POLAR, both at 50° and 15 psi N_2).

The disulfide was collected by filtration and was found to be identical with authentic material in mixture m.p.. The yield and m.p. of the disulfide obtained in these four runs were: run 11, 0.257 g, m.p. $234-236^{\circ}$; run 12, 0.268 g, m.p. $232-235^{\circ}$; run 13, 0.341 g; run 14, 0.352 g, m.p. $234-236^{\circ}$.

Evaporation of the filtrates gave the crude sulfides. Run 11, 0.775 g; run 12, 0.751 g; run 13, 0.640 g; run 14, 0.664 g. The pentachlorophenyl sulfides from butane (VIII and IX) were obtained as an oil. Those from isobutane (X and XI) were obtained as an oil which solidified on standing.

The isomer ratios were determined by nmr. By comparing the ArS-C-H signal of IX (τ 6.65, multiplet) to the ArS-CH$_2$- signal of VIII (τ 7.12, triplet) in CCl_4 solvent, the ratio of IX/VIII was found to be 4.5 for run 11 and 4.1 for run 12. Similarly by comparing the t-butyl singlet of XI (τ8.82) to the gem-dimethyl doublet of X (τ9.14) in benzene solvent, the ratio of XI/X was found to be 2.1 for run 13 and 2.2 for run 14.

The identity of the butyl pentachlorophenyl sulfides was partially established by addition of the authentic compounds to the

mixtures and reobtaining the nmr spectra. Further identification was accomplished by glpc retention time comparison with authentic VIII, IX, X, XI (model 202, 5' SE-30 at 220-240°, 60 ml He/min). The area ratios were in agreement with the ratios determined from the nmr spectra. Samples were collected by preparative glpc for comparison of IR spectra and were found to be identical to authentic materials in this respect. Mass spectra were obtained for each of the sulfides collected by glpc. Each spectrum had a set of parent peaks at m/e 336, 338, 340 and 342 in the expected ratios for five chlorine atoms ($C_6{}^{35}Cl_5C_4H_9$ = 336). The base peak for each of the isomers was at m/e 57 (C_4H_9), and was very prominent in the spectrum of XI.

Hexachlorobenzene (identified by glpc retention time and by the mass spectrum of a collected sample) was also present in the mixtures. It comprised about 4% (by peak area) for runs 11 and 12, and 5% for runs 13 and 14.

Pentachlorothiophenol was estimated by the acetylation method previously described. For both run 12 and run 14 none of the acetate could be detected by glpc. Under the analytical conditions employed the upper limit for the yield of pentachlorothiophenol was 0.5%. Run 12 could be analyzed under the glpc conditions as used before. Run 14 was analyzed on the model 600-D using the 5' QF-1 column at 200° and 10 psi N_2.

IX.   PHOTOCHLORINATION OF NORMAL BUTANE AND ISO-

       BUTANE

Butane (2 ml, ca. 20 mmole) was photochlorinated at 40° with 2.0 mmole of chlorine in sealed, degassed ampoules with 4.0 ml of carbon tetrachloride as solvent.

Analysis by glpc (20' SF-96 column) gave, for three reactions, sec-C_4H_9Cl/n-C_4H_9Cl = 1.65 $\pm$ 0.07 for a primary : secondary ratio of 2.5 $\pm$ 0.1.

Similarly photochlorination of 20 mmole of isobutane with 1.7 mmole of chlorine in 4.0 ml of carbon tetrachloride gave, for two reactions, t-C_4H_9Cl/iso-C_4H_9Cl = 0.358 $\pm$ 0.016 for a primary : tertiary ratio of 3.2 $\pm$ 0.15.

X.   REACTION OF ISOBUTANE WITH PBSC-CHLORINE (RUNS 15

       AND 16)

Two reactions were run at 40°. Each reaction mixture consisted of isobutane (5 ml, ca. 50 mmole), PBSC (run 15, 0.536 g, 1.69 mmole; run 16, 0.507 g, 1.60 mmole), chlorine (1.37 mmole), Freon 112 (1.00 mmole) and carbon tetrachloride (10.0 ml). Irradiation times of 8-9 hr were required for completion of reaction.

The alkyl chlorides were quantitated by glpc as before (runs 13 and 14).

The yield, melting point and mixture melting point (with authentic material) of the disulfide (I) were: run 15, 0.116 g, 234-

236°, $235\text{-}237^{\circ}$; run 16, 0.113 g, $235\text{-}237^{\circ}$, — .

The yield of crude sulfide was 0.423 g (1.25 mmole) for run 15 and 0.399 g (1.18 mmole) for run 16.

The nmr spectra (CCl_4) of the sulfides were qualitatively identical to those previously obtained for the sulfides from runs 13 and 14. Since the spectra did not contain any signals below τ 7.1 it was concluded that no chlorination of the sulfides had occurred. The ratio of XI/X was 1.44 for run 15 and 1.41 for run 16.

Hexachlorobenzene was estimated by glpc analysis as before and found to comprise 4-5% (by peak area) of the crude sulfide mixtures. The peak area ratio of XI/X was about 1.3 : 1 for both runs.

XI. PHOTOCHLORINATION OF NORMAL BUTANE (RUNS 17 AND 18) AND ISOBUTANE (RUNS 19 AND 20) IN THE PRESENCE OF n-BUTYL PENTACHLOROPHENYL SULFIDE (VIII).

Each reaction mixture contained 2 ml (20 mmole) of hydrocarbon (3.3 M), 1.20 mmole of chlorine (0.20 M), 0.60 mmole of VIII (0.10 M), 2.00 mmole of Freon 112 and 4.0 ml of carbon tetrachloride. The chlorinations were carried out at 40° and required about 0.25 hr of irradiation. The alkyl chlorides were analyzed by glpc as before. For runs 17 and 18, the molar ratio sec-C_4H_9Cl/ n-C_4H_9Cl was 1.78 ± 0.06 for a primary : secondary ratio 2.7 ± 0.1. The total yield of alkyl chlorides was 0.72 mmole or about 60% of theoretical based on chlorine.

The reaction mixtures from runs 17 and 18 were combined and the solvent removed to give 0.454 g of colorless oil. When the nmr spectrum of this oil was obtained in carbon tetrachloride solution it showed that the sulfide had undergone chlorination. The signal at τ 4.6 (triplet) was assigned to the α-chlorinated product, and the signal at τ 5.8 was assigned to the β-chlorinated product. The ratio of α-chlorination to β-chlorination was about 2 : 1. From a comparison of the integrated intensities of the chlorinated sulfides and the unchlorinated starting material it was estimated that about 40% of the sulfide had been chlorinated. Because the α, α-dichlorosulfide could not be observed by nmr, it was not known for certain if any dichlorosulfide was produced in the reaction.

Runs 19 and 20 were analyzed in the same way. The ratio of $\underline{t}$-C_4H_9Cl to $\underline{iso}$-C_4H_9Cl was 0.388 ± 0.023 for a primary : tertiary ratio of 3.5 ± 0.2. The total yield of chlorides was 0.60 mmole, about 50% of theoretical. The combined yield of (chlorinated) sulfides was 0.450 g. The nmr spectrum was qualitatively identical to that obtained before for the sulfides from runs 17 and 18. Again the ratio of α-chlorination to β-chlorination was 2 : 1. About 50% of the sulfide had been chlorinated.

XII. PHOTOLYSIS OF I IN ISOBUTANE-CARBON TETRACHLORIDE (RUN 21)

Isobutane (5 ml, 50 mmole), I (0.28 g, 0.50 mmole) and 10 ml of carbon tetrachloride were placed in an ampoule, degassed and

sealed under vacuum.

Because of the low solubility of I in the mixture at 40°, the reaction was carried out at 80°. After 50 hr of irradiation all of I had disappeared. The ampoule was cooled in liquid nitrogen, opened and the solvent removed to give 0.32 g of tan-colored solid. Analysis by glpc (model 202, 5' SE-30 at 210°, 60 ml He/min) showed three products identified by retention times as VI, XI and X in order of elution. The ratio of XI to X was ca. 40 : 1. Samples of VI and XI were collected for comparison of IR spectra (CS_2) with authentic materials.

The solid was dissolved in hot benzene and let stand over-night to deposit 0.04 g of I, m.p. $234-236^{\circ}$. The recovery of soluble material was 0.26 g. The ratio of VI to XI was determined from the nmr spectrum (benzene) of this soluble portion, and was found to be 45 : 55. The S-H proton of VI appeared at τ 5.68 (compared to τ 5.70 for authentic VI), and the t-butyl singlet of XI appeared at τ 8.86 (compared to τ 8.82 for authentic XI). The yield of VI calculated from these data was 0.39 mmole and of XI 0.46 mmole or 78% and 92% respectively based on disulfide.

XIII. PHOTOLYSIS OF I IN CYCLOHEXANE-CARBON TETRA-CHLORIDE (RUN 22)

The reaction was carried out as above using 0.28 g (0.50 mmole) of I, 2.0 ml (19 mmole) of research grade cyclohexane and 3.0 ml of carbon tetrachloride. Irradiation at 80° for 150 hr gave only

partial reaction; <u>i.e.</u>, much of the disulfide remained undissolved.

After standing at room temperature for several hr, the ampoule was opened and unreacted I filtered off (0.242 g, m.p. 235-237°).

To the soluble portion (0.035 g after removal of solvent) was added 0.010 g (0.035 mmole) of hexachlorobenzene as an internal standard. After acetylation (0.5 ml acetyl chloride, 0.5 ml of pyridine, 10 ml carbon tetrachloride, heated 0.5 hr under reflux) and analysis by glpc the yield of VII was 0.024 mmole and of III 0.025 mmole, or about 5% of each based on starting disulfide. Samples of III and VII were collected for comparison of IR spectra (CS$_2$) with the authentic materials, and were found to be identical.

XIV. BENZOYL PEROXIDE INITIATED REACTION OF BISPENTA-
        CHLOROPHENYL DISULFIDE (I) AND ISOBUTANE (RUN 23)

Bispentachlorophenyl disulfide (0.28 g, 0.50 mmole), benzoyl peroxide (0.012 g, 0.050 mmole), isobutane (5 ml, 50 mmole) and carbon tetrachloride (10 ml) were placed in an ampoule, degassed and sealed under vacuum. The ampoule was heated at 80° in the dark for 2 days. After freezing in liquid nitrogen, the ampoule was opened and unreacted disulfide (0.18 g, m.p. 235-237°) was filtered off. Removal of hydrocarbon and solvent from the filtrate afforded 0.113 g of solid. A further 0.024 g of unreacted I (m.p. 234-236°) was removed from this solid by crystallization from benzene (2 ml). The soluble portion weighed 0.090 g. Analysis by glpc (model 202, 5'

SE-30 at 235°, 60 ml He/min) showed VI, XI and X which were identified by their retention times. The ratio of XI to X was about 20 : 1. The nmr spectrum (benzene) showed a singlet for VI at τ5.76, a singlet for XI at τ 8.87 and a gem-dimethyl doublet for X at τ9.17. The ratio of VI to XI to X was about 10 : 15 : 1. The mmolar (%) yields calculated from the weight of isolated material and the nmr ratios were: VI, 0.12 mmole (24%); XI, 0.17 mmole (34%); X, 0.01 mmole (2%).

XV. BENZOYL PEROXIDE INITIATED REACTION OF BISPENTA-CHLOROPHENYL DISULFIDE (I) AND CYCLOHEXANE (RUN 24)

Bispentachlorophenyl disulfide (0.28 g, 0.50 mmole), benzoyl peroxide (0.012 g, 0.050 mmole), research grade cyclohexane (5 ml, 46 mmole) and carbon tetrachloride (10 ml) were placed in an ampoule, degassed and sealed under vacuum. The ampoule was heated in the dark at 80° for 2 days. After cooling, the ampoule was broken open and unreacted I (0.21 g, m.p. 235 - 237°) was filtered off. Removal of hydrocarbon and solvent from the filtrate gave 0.083 g of solid. One-half of this solid (0.042 g) was acetylated by the same procedure as was used to analyze the products from run 21 (photoinitiated reaction of I and cyclohexane). Hexachlorobenzene (0.010 g, 0.035 mmole) was again used as the internal standard; VII and III were identified by glpc retention times. The total yields (corrected to analysis of all the material) estimated by this method were: VI, 0.01 mmole (2%); III, 0.09 mmole (18%).

XVI. PHOTOLYSIS OF PBSC IN CARBON TETRACHLORIDE

PBSC (0.487 g, 1.54 mmole) was photolyzed at 40° for 24 hr in a sealed, degassed ampoule using 5 ml of carbon tetrachloride as solvent. The volatile components were removed by vacuum transfer at room temperature and 0.05 mm. By iodometric titration, 0.10 mmole of active halogen was found in the distillate, and 0.94 mmole was found in the residue.   After titration, the organic layer was removed and evaporated leaving a pale yellow solid. Analysis of this solid by glpc (model 600-D, 5' SE-30 at 200°, 15 psi N_2) showed hexachlorobenzene as the sole volatile product. By sublimation at 150° and 15 mm, 0.075 g (17%) of hexachlorobenzene was obtained m.p. $223-226^O$ (sealed tube). After one crystallization from carbon tetrachloride it had m.p. $228-229^O$ (sealed tube) and mixture m.p. with authentic material $228-229^O$ (sealed tube). The IR spectrum (nujol mull) was identical to that of authentic material.

XVII. ATTEMPTED REACTION OF PBSC WITH ANHYDROUS
HYDROGEN CHLORIDE

Anhydrous hydrogen chloride was bubbled slowly through PBSC (0.200 g) in 2.0 ml of carbon tetrachloride for 0.5 hr at 0°.   About one-half of the solvent was vacuum transferred at room temperature and 0.1 mm.   The distillate smelled strongly of hydrogen chloride, but contained no active halogen when tested with potassium iodide in aqueous acetic acid.   The residue from the vacuum transfer was titrated iodometrically and found to possess $>99.5\%$ of the original active halogen.

In another experiment carried out at room temperature in the dark, anhydrous hydrogen chloride was passed through a solution of 0.5 g of PBSC in 25 ml of dry carbon tetrachloride for 0.5 hr. The PBSC solution was contained in a three-neck flask equipped with gas inlet and condenser set for distillation. The distillation receiver contained 5 ml of carbon tetrachloride and was cooled in ice. After passage of hydrogen chloride into the solution was stopped, 15 ml of the solvent was distilled after a waiting period of 0.25 hr. The distillate was colorless and smelled strongly of hydrogen chloride. It gave a negative test for molecular chlorine when tested with potassium iodide in aqueous acetic acid.
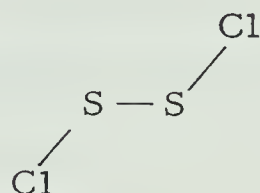
PART   TWO

SULFUR   MONOCHLORIDE

INTRODUCTION

A linear structure has been determined for sulfur monochloride by electron diffraction (46).

$$S - S \diagup_{Cl}^{Cl}$$

The reactions of the reagent with organic substrates have recently been reviewed (47). This review article describes the reagent as finding wide use in industry for the manufacture of oil additives, vulcanization of rubber, cross-linking of polymers and the manufacture of sulfur containing dyes. This review states that patents on the use of sulfur monochloride have averaged eight per year in recent years. As a consequence much of the chemistry of the reagent is to be found in the patent literature. The review article also reveals that until 1962 little was known of the free-radical chemistry of sulfur monochloride.

More recently, Müller and Schmidt have reported their study of the free-radical reactions of sulfur monochloride (10) and the closely related sulfur dichloride (9) with hydrocarbons. The former reagent yielded, under their reaction conditions, alkylthiosulfenyl chlorides (RSSCl, alkylchlorodisulfanes*) and the latter reagent yielded alkylsulfenyl chlorides (RSCl, alkylchloromonosulfanes*). The reactions were initiated by ultraviolet irradiation in a continuous

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* The nomenclature used by Müller and Schmidt (9, 10).

reaction system where reactants were recycled after one hour of irradiation under an atmosphere of nitrogen. Sweeping the reaction mixture with nitric oxide instead of nitrogen caused a decrease in the evolution of hydrogen chloride (9b). This, plus the initiation by ultraviolet light, constituted evidence for proposing the reactions to be free-radical processes.

Müller and Schmidt reported a primary : secondary selectivity of 1 : 3 in the reactions of both reagents with n-pentane, n-hexane and n-heptane. Primary : secondary selectivities of 1 : 3.5 for n-butane (48) and 1 : 3.6 for n-pentane (16) have been obtained in photochlorination reactions using molecular chlorine. The close agreement of these selectivities suggests chlorine atoms are the abstracting radicals.

Müller and Schmidt did not investigate the free-radical reactions of the alkylthiosulfenyl chlorides. In the authors' words:

> "... the alkylchlorodisulfanes react further, under the influence of light in the presence of hydrocarbons, to mixtures which are difficult to identify." (10)

By using a continuous reaction unit subsequent reaction of the alkylthiosulfenyl chlorides was minimized (10). Because of the reactivity of these alkylthiosulfenyl chlorides, the authors found it necessary to characterize them mainly in the form of derivatives e.g., as the thiocyanates and dimethylamino derivatives.

$$RSSCl + 2\,KCN \longrightarrow RSCN + KCN + KCl$$

$$RSSCl + 2\,HN(CH_3)_2 \longrightarrow RSS-N(CH_3)_2 + H_2N(CH_3)_2Cl$$
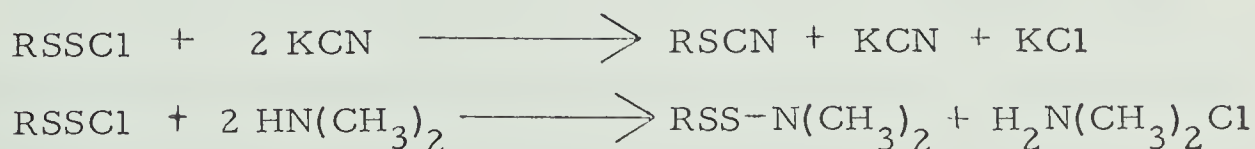
The main side reaction encountered in the reaction of sulfur monochloride with hydrocarbons was formation of elemental sulfur. Small amounts of alkyl chlorides were obtained, but were not quantitated.

Müller and Schmidt (10) suggested a mechanism where the preferred initial step is homolytic cleavage of the S-Cl bond.

$$S_2Cl_2 \xrightarrow{\quad h\nu \quad} \cdot S_2Cl + Cl\cdot \qquad (1)$$

Hydrogen abstraction was suggested to be by chlorine atoms.

$$RH + Cl\cdot \longrightarrow R\cdot + HCl \qquad (2)$$
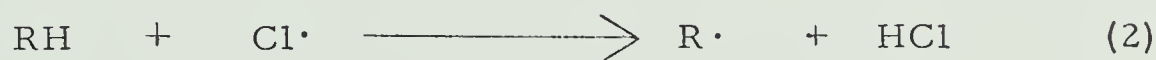
Two possibilities were proposed for formation of the alkylthiosulfenyl chlorides:

$$R\cdot + S_2Cl_2 \longrightarrow RS_2Cl + Cl\cdot \qquad (3)$$
$$R\cdot + \cdot S_2Cl \longrightarrow RS_2Cl \qquad (4)$$
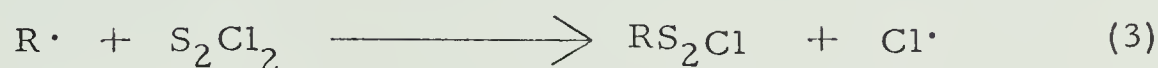
Alkyl chlorides were suggested to arise from the coupling reaction:

$$R\cdot + Cl\cdot \longrightarrow RCl \qquad (5)$$

This mechanism did not attempt to distinguish between a chain process involving a radical displacement reaction (equation 3) and a nonchain process involving a radical coupling reaction (equation 4).

This study was begun with the intention of investigating the reactions of sulfur monochloride with hydrocarbons in systems taken to complete reaction. By so doing it was hoped that additional

information could be gained regarding the mechanism of the reaction and that this information could be related to the results of Müller and Schmidt and thereby provide a fuller understanding of the reactions of this interesting and synthetically useful reagent.

The general approach to the problem paralleled that used for pentachlorobenzenesulfenyl chloride in that emphasis was placed on the need for determining the chain nature of the reaction, establishing a material balance and determining the selectivity of the reagent in order to determine the hydrogen abstracting species.

RESULTS

I.   INITIATION-INHIBITION STUDIES.

Initiation-inhibition studies were carried out in an effort to establish the chain or nonchain nature of the reaction using cyclohexane as the substrate.   The results in Table I are expressed as the per cent of active halogen remaining as determined by iodometric titration.

Although atmospheric amounts of oxygen did not inhibit the reaction (compare degassed and not degassed, 40°, hν in Table I) the reaction mixtures of sulfur monochloride and hydrocarbons described in the subsequent work were degassed prior to irradiation.

II.   REACTION OF SULFUR MONOCHLORIDE WITH CYCLO-
HEXANE.

Cyclohexane was the substrate chosen for establishment of a material balance.   At 40° the photoinitiated reaction of sulfur monochloride with cyclohexane yielded a complex product mixture.   The inorganic products were hydrogen chloride and elemental sulfur (symbolized by S° throughout the text). Hydrogen chloride yields are summarized in Table II.   The yield (as mole/mole of sulfur monochloride) varied little with variations in the molar ratio of sulfur monochloride to cyclohexane.

TABLE I

THE EFFECT OF INITIATORS AND INHIBITORS ON THE REACTION

OF SULFUR MONOCHLORIDE WITH CYCLOHEXANE.[a]

Conditions	Time (hr)	Per cent of Active Halogen Remaining[b]
Degassed, 40°, dark	70	100
Degassed, 40°, dark plus AIBN[c] (8 mole %)	70	>99
Degassed, 40°, hν	70	1
Degassed, 80°, dark	9	100
Degassed, 80°, dark plus benzoyl peroxide		
(2 mole %)	9	99
(5 mole %)	9	97
(10 mole %)	9	94
Degassed, 40°, hν [d]	19	72
	41	39
Not degassed, 40°, hν [d]	19	71
	41	40
Degassed, 40°, hν, plus nitric oxide (20-30 mole %)[d]	19	70
	41	42

[a] Each reaction consisted of a solution of sulfur monochloride (0.3 M) and cyclohexane (3.0 M) in carbon tetrachloride. The reactions were carried out in sealed Pyrex ampoules.

[b] Determined by iodometric titration.

[c] AIBN is the abbreviation used for azobisisobutyronitrile.

[d] Ampoules were irradiated in a Rayonet merry-go-round apparatus to ensure uniform irradiation of all samples.

TABLE II

HYDROGEN CHLORIDE YIELDS IN THE PHOTOINITIATED REACTION
OF SULFUR MONOCHLORIDE WITH CYCLOHEXANE AT 40°.[a]

S_2Cl_2, M	C_6H_{12}, M	Number of Reactions	moles HCl/mole S_2Cl_2 [b]
0.094	2.8	2	1.39 ± 0.01
0.113	2.8	1	1.39
0.296	2.8	2	1.48 ± 0.01
0.300	2.7	2	1.46 ± 0.02

[a] Carbon tetrachloride solvent.

[b] Determined by titration of hydrogen chloride with standard
sodium hydroxide to a phenolphthalein end point.   Experimental
uncertainties are standard deviations.

The yield of elemental sulfur was determined by isolation of

elemental sulfur from the reaction mixtures employing column

chromatography on silica gel.   Of the sulfur originally present in

the sulfur monochloride, 30-35% appeared as elemental sulfur at

completion of reaction.

Analysis by gas liquid partition chromatography (glpc) allowed

identification and quantitation of the volatile organic products.   These

consisted of: cyclohexyl chloride (I);   traces of cyclohexyl mercaptan

(II);   a series of at least eight components present in very minor

amounts and presumed to be polychlorinated cyclohexanes;   an

unresolved mixture (III) of two compounds $C_{12}H_{22}S$ (IIIa) and $C_{12}H_{16}S$ (IIIb) tentatively assigned as dicyclohexyl and phenyl cyclohexyl sulfides; a compound $C_{12}H_{15}ClS$ (IV) for which the probable structure was that of o-chlorophenyl cyclohexyl sulfide on the basis of mass, infrared (IR) and ultraviolet (uv) spectral data; and dicyclohexyl disulfide (V).

The yield of cyclohexyl chloride was determined by glpc for reaction mixtures with differing initial concentrations of sulfur mono-chloride. As can be seen from Table III, within experimental error, the yield of cyclohexyl chloride was independent of the concentration of sulfur monochloride.

TABLE III

CYCLOHEXYL CHLORIDE YIELDS IN THE PHOTOINITIATED
REACTION OF SULFUR MONOCHLORIDE WITH CYCLOHEXANE
AT 40°.[a]

S_2Cl_2, M	C_6H_{12}, M	Number of Reactions	mole $C_6H_{11}Cl$/mole S_2Cl_2
0.0985	2.8	1	0.309
0.113	2.8	3	0.301 ± 0.006
0.295	2.8	2	0.289 ± 0.002
0.301	2.8	3	0.289 ± 0.009

[a] Carbon tetrachloride solvent.

From the glpc analysis of the reaction products the yield of dicyclohexyl disulfide was 0.08 mole/mole of sulfur monochloride, and the yields of the two minor components III and IV were 0.005 and 0.01 mole/mole of sulfur monochloride respectively.

The remainder of the products appeared as dicyclohexyl poly-sulfides* which could not be analyzed by glpc. They were estimated by nuclear magnetic resonance (nmr), and as cyclohexyl mercaptan after reduction with lithium aluminum hydride. The yield of dicyclo-hexyl polysulfides including dicyclohexyl disulfide was 0.30 mole/mole of sulfur monochloride and the yield of cyclohexyl mer-captan after reduction was 0.608 ± 0.020 mole/mole of sulfur mono-chloride.

To complete the material balance, the amount of cyclohexane consumed per mole of sulfur monochloride reaction was determined using glpc. The results are summarized in Table IV.

TABLE IV

CYCLOHEXANE CONSUMPTION IN THE PHOTOINITIATED REACTION OF SULFUR MONOCHLORIDE WITH CYCLOHEXANE AT 40° (CARBON TETRACHLORIDE SOLVENT AND INTERNAL STANDARD).

S_2Cl_2, M	C_6H_{12}, M	Number of Reactions	mole cyclohexane reacting /mole S_2Cl_2
0.299	2.645	2	1.02 ± 0.05
0.298	2.575	2	1.05 ± 0.08
0.301	2.820	3	0.92 ± 0.14
		Average =	1.00 ± 0.10

* Throughout the text polysulfides are designated by the symbols RS_xR, RS_mR or RS_nR depending on the context.

III.   REACTION OF SULFUR MONOCHLORIDE WITH CYCLO-

PENTANE.

The reaction of sulfur monochloride with cyclopentane at 40°

was accompanied by formation of colored byproducts.   The reactions

were stopped short of completion and analyzed for active halogen

remaining, hydrogen chloride, cyclopentyl chloride and dicyclopentyl

polysulfides.   Table V summarizes the product yields.

TABLE V

PRODUCT YIELDS IN THE PHOTOINITIATED REACTION OF SULFUR

MONOCHLORIDE WITH CYCLOPENTANE   AT 40°.[a]

	mole/mole S_2Cl_2				
active -Cl	HCl	C_5H_9Cl	Total chlorine (% of Cl)	C_5H_9SH[b]	$C_5H_9S_x$-[c]
0.19	1.31	0.24	1.74 (87)	0.45	....
0.24	1.27	0.24	1.75 (88)	0.40	....
0.19	1.25	0.24	1.68 (84)	....	0.50

[a] The reaction mixtures consisted of 5.00 ml of a carbon tetra-
chloride solution of sulfur monochloride (0.30 M), cyclopentane
(3.4 M) and the internal standard Freon 112 (0.21 M).

[b] Determined by glpc after reduction of the polysulfides with lithium
aluminum hydride.

[c] Determined by nmr.

IV.   REACTION OF SULFUR MONOCHLORIDE WITH BUTANE
       AND ISOBUTANE.

Sulfur monochloride was reacted with butane and isobutane
so that the selectivity of the hydrogen abstracting radical could be
determined from the product distribution obtained.

Due to formation of colored material (0.004 g from 3 mmole
of sulfur monochloride) in the butane reactions it was difficult to tell
when the reactions were completed.   The percentage of reaction was
determined by iodometric titration.   The results summarized in
Table VI are for reactions taken to 90-100% completion.   The yields
of products are in mole/mole of sulfur monochloride and are corrected
to 100% reaction.

Sulfur monochloride and isobutane reacted smoothly at 40°.
All reactions were taken to 100% completion.   The product yields
are presented in Table VII.

V.   DIRECT ANALYSIS OF POLYSULFIDE COMPOSITION.

Dicyclohexyl tetrasulfide was synthesized with the intention of
using it for comparison with the polysulfides from reaction of cyclo-
hexane with sulfur monochloride.   No analytical means could be
found which would allow an estimation of the tetrasulfide.   Dicyclo-
hexyl di- and tetrasulfide possessed identical R_f values when subjected
to thin-layer chromatography in the solvent system used.   Their IR
spectra were identical with respect to position of absorption bands.
A parent ion could not be obtained for the tetrasulfide when subjected

TABLE VI

PRODUCT YIELDS IN THE PHOTOINITIATED REACTION OF SULFUR MONOCHLORIDE WITH BUTANE AT 40°.[a]

		mole/mole S_2Cl_2			
n-C_4H_9Cl	sec-C_4H_9Cl	n-$C_4H_9S_x$-[b]	sec-$C_4H_9S_x$-[b]	n-C_4H_9SH[c]	sec-C_4H_9SH[c]
0.08	0.20	0.28	0.45	....	....
0.06	0.19	0.21	0.43	....	....
0.09	0.22	0.28	0.54	....	....
0.08	0.21	....	....	0.23	0.45

a   Reaction mixtures consisted of 5 ml of hydrocarbon (ca. 50 mmole) and 10.0 ml of a carbon tetrachloride solution 0.3 M in sulfur monochloride (3.0 mmole) and 0.2 M in Freon 112 as internal standard (2.0 mmole).

b   Determined by nmr.

c   As mercaptan after reduction with lithium aluminum hydride.

TABLE VII

PRODUCT YIELDS IN THE PHOTOINITIATED REACTION OF SULFUR MONOCHLORIDE WITH

ISOBUTANE AT 40°.[a]

		mole/mole S_2Cl_2			
iso-C_4H_9Cl	t-C_4H_9Cl	iso-$C_4H_9S_x$-[b]	t-$C_4H_9S_x$-[b]	iso-C_4H_9SH[c]	t-C_4H_9SH[c]
0.19	0.14	0.47	0.20	....	....
0.17	0.16	0.50	0.19	....	....
0.18	0.15	0.53	0.22	....	....
0.19	0.14	....	....	0.45	0.18

a   Reaction mixtures consisted of 5 ml of hydrocarbon (ca. 50 mmole) and 10.0 ml of a carbon tetrachloride solution 0.3 M in sulfur monochloride (3.0 mmole) and 0.2 M in Freon 112 as internal standard (2.0 mmole).

b   Determined by nmr.

c   As mercaptan after reduction with lithium aluminum hydride.

to mass spectral analysis.

An examination by 100 megacycle nmr of the polysulfides produced from reaction of sulfur monochloride and isobutane gave more satisfactory results. At the higher resolution afforded by 100 megacycle nmr the t-butyl singlets (τ8.48-8.65) were resolved and could be assigned to the various di-t-butyl- and t-butyl-iso-butyl polysulfides by comparison of chemical shifts with di-t-butyl di- and tetrasulfide and by consulting known work (the assignment of chemical shifts is described in the Experimental section). The mole fractions of Table VIII are for the corresponding polysulfides and were obtained by comparing the peak height of the t-butyl singlet of each polysulfide to the total value obtained by summing the peak heights for all the singlets (τ 8.48-8.65).

Irradiation of di-t-butyl tetrasulfide at 40° in carbon tetra-chloride for 150 hr gave about 5% of disproportionation of the tetra-sulfide to other polysulfides. This was much less than the extent of disproportionation required to give the distribution of polysulfides represented by the mole fractions in Table VIII. Since no blank was run in the dark it was impossible to tell whether the disproportion-ation that did occur in the above mentioned experiment was due to thermolysis or photolysis. The desired point was nonetheless demonstrated, namely that thermal or photolytic disproportionation of tetrasulfides was not sufficient to account for the distribution of polysulfides obtained from reaction of sulfur monochloride and iso-butane.

TABLE VIII

MOLE FRACTIONS[a] OF THE DI-t-BUTYL- AND t-BUTYL-iso-BUTYL POLYSULFIDES FROM REACTION OF SULFUR MONO-CHLORIDE WITH ISOBUTANE.

RS_mR[b]	mole fraction		RS_nR'[c]
m	RS_mR	RS_nR'	n
2	0.01	0.11	2
3	0.11	0.20	3
4	0.26	0.05	4
5	0.07	0.04	5
6	0.05	0.05	6
7	0.05		

a   Defined in the text.

b   R equals t-C_4H_9.

c   R' equals iso-C_4H_9.

VI.   RELATIVE REACTIVITIES OF HYDROCARBONS TOWARD
       SULFUR MONOCHLORIDE.

The relative reactivities of cyclohexane, cyclopentane, 2,3-dimethylbutane, toluene and norbornane toward sulfur monochloride were obtained from competition experiments analyzed for disappearance of hydrocarbons.   These relative reactivities were used to augment the selectivities previously obtained.   Competition experiments have the advantage that the products can undergo subsequent (side) reactions and the values obtained will not be affected because they are based solely on the disappearance of hydrocarbon.   Table IX contains the results of these competition experiments.   Because chlorine atoms were suggested as the hydrogen abstracting species (10) the results obtained here are compared in Table IX with those of Russell, Ito and Hendry (48) and of Walling and Mayahi (49) for the relative reactivities of the same hydrocarbons toward chlorine atoms.

VIII.   CYCLOHEXYLTHIOSULFENYL CHLORIDE (VI) AS AN
         INTERMEDIATE IN THE REACTION OF SULFUR MONO-
         CHLORIDE WITH CYCLOHEXANE.

A reaction mixture of cyclohexane and sulfur monochloride was reacted to partial completion and was then treated with dimethyl-amine.   After isolation of the product by distillation a mixture was obtained of which the dimethylamino derivative of VI was the major component (about 80%).   It could be identified by its R_f value when

TABLE IX

RELATIVE REACTIVITIES OF VARIOUS HYDROCARBONS TOWARD
SULFUR MONOCHLORIDE AT 40° COMPARED WITH RELATIVE
REACTIVITIES OF THE SAME HYDROCARBONS TOWARD CHLORINE
ATOMS.

Hydrocarbon	Relative Reactivity per Molecule		
	This Work[a]	Ref. 48[b]	Ref. 49[c]
cyclohexane	1.00	1.00	1.00
cyclopentane	0.82 ± 0.05	0.86	0.75 ± 0.01
2,3-dimethylbutane	0.69 ± 0.03	0.61	0.86
toluene	0.135 ± 0.015	0.13	....
norbornane	0.70 ± 0.06	....	0.75 ± 0.05

[a] Values obtained at 40°, Freon 112 as solvent (3 M). Experimental uncertainties are standard deviations for two reactions.

[b] Values obtained at 40°, reactants as solvent.

[c] Values obtained at 68°, carbon tetrachloride as solvent (5 M).

the mixture was subjected to tlc analysis, and from the mass spectrum

of the mixture.   On the basis of tlc analysis and the mass spectrum

of the mixture dicyclohexyl disulfide was a minor component (5-10%)

of the mixture.

Cyclohexylthiosulfenyl chloride was prepared and treated

with cyclohexane at 40°.   Degassed carbon tetrachloride solutions

of cyclohexylthiosulfenyl chloride (0.25 M) and cyclohexane (2.8 M)

were irradiated and the products analyzed qualitatively and quanti-

tatively by the same procedures as used for analyzing the sulfur

monochloride-cyclohexane reactions.

The yields of products (mole/mole of cyclohexylthiosulfenyl

chloride) were as follows: hydrogen chloride, 0.79;   cyclohexyl

chloride, 0.13 ± 0.003;   dicyclohexyl disulfide, 0.39 ± 0.01;

dicyclohexyl polysulfide including disulfide, 0.66 (by nmr);   cyclo-

hexyl mercaptan after reduction, 1.20 ± 0.08.   Elemental sulfur was

not produced in these reactions as shown by its absence when the

reaction mixtures were subjected to tlc analysis.

When the reaction of cyclohexylthiosulfenyl chloride (0.25 M)

with cyclohexane (2.8 M) was carried out in the presence of added

elemental sulfur (0.8 equivalents) the yields (mole/mole of cyclo-

hexylthiosulfenyl chloride) were as follows: cyclohexyl chloride,

0.11 ± 0.01; dicyclohexyl disulfide, 0.31 ± 0.02;   cyclohexyl mercap-

tan after reduction, 1.27 ± 0.04.

DISCUSSION

The results of initiation-inhibition studies (Table I) showed that light effectively initiated the reaction of sulfur monochloride with cyclohexane. Attempts to initiate the reaction with small amounts of azobisisobutyronitile and benzoyl peroxide were unsuccessful, and oxygen and nitric oxide did not inhibit the photoinitiated reaction. These results can be interpreted in two ways. First, the reaction may not be a chain reaction and therefore the products come mainly from radical coupling reactions. Second, the reaction may be a strongly inhibited chain reaction, i.e., the products do arise from displacement reactions but the chain length is decreased due to inhibition. Certainly in the later stages of reaction inhibition was likely because of the presence of elemental sulfur which is known to be a good radical scavenger (50).

The product yields obtained from analysis of reactions of sulfur monochloride and of cyclohexylthiosulfenyl chloride (VI) with cyclohexane are summarized in Table X. Material balances of 88% and 92% respectively were obtained on chlorine for the two reagents, based on the yield of hydrogen chloride and cyclohexyl chloride. In the sulfur monochloride-cyclohexane reaction 90% of the hydrocarbon reacting appeared as the monosubstituted products cyclohexyl chloride and dicyclohexyl di- and polysulfides. The overall reaction of sulfur monochloride with hydrocarbons can therefore be represented by equation 6.

TABLE X

COMPARISON OF PRODUCT YIELDS IN THE PHOTOINITIATED REACTIONS OF SULFUR

MONOCHLORIDE AND CYCLOHEXYLTHIOSULFENYL CHLORIDE (VI) WITH

CYCLOHEXANE AT 40°.

Reactants (moles)		Moles of Product						
		C_6H_{12}	$C_6H_{11}Cl$	$C_6H_{11}S_2C_6H_{11}$	$C_6H_{11}S_xC_6H_{11}$[a] (x≥2)	$C_6H_{11}SH$[a] after reduction	HCl	Elemental Sulfur[b]
S_2Cl_2 (1.00)	C_6H_{12} (10.0)	9.0	0.29 ±0.01	0.08 ±0.004	0.30	0.61 ±0.02	1.47	0.30-0.35
VI (1.00)	C_6H_{12} (11)	-	0.13 ±0.003	0.39 ±0.01	0.66	1.20 ±0.08	0.79	none detectable by tlc
VI (1.00)	C_6H_{12} (11) sulfur (0.8 equivalents)	-	0.11 ±0.01	0.31 ±0.02	-	1.27 ±0.004	-	-

a The yield of $C_6H_{11}SH$ after reduction should be twice that of $C_6H_{11}S_xC_6H_{11}$.

b Fraction of sulfur originally present as sulfur monochloride.

88

$$S_2Cl_2 + RH \xrightarrow{\;h\nu\;} RCl + RS_xR + HCl + S^{\circ} \qquad (6)$$

$$(x \geqslant 2)$$
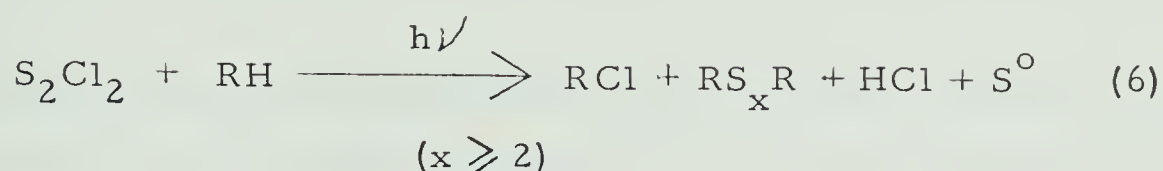
Sulfur monochloride was reacted with cyclopentane, butane and isobutane and the reaction mixtures were analyzed for yields of alkyl chlorides and dialkyl polysulfides. Butane and isobutane were used as substrates so that the selectivity of sulfur monochloride could be determined.

Müller and Schmidt (10) proposed that hydrogen abstraction was by chlorine atoms (equation 2) on the basis of the product distribution observed for the alkylthiosulfenyl chlorides which they obtained. Their observation that sulfur monobromide (S_2Br_2) was unreactive in photoinitiated reactions with hydrocarbons lent support to their proposal.

Because the reactions described here were for systems taken to complete reaction it was felt that the selectivity of sulfur monochloride should be determined since the intermediate alkylthiosulfenyl chlorides were also involved in the reactions. The primary : secondary : tertiary selectivity of sulfur monochloride with butane and isobutane was 1 : 3.1 : 4.6 as calculated from the product yields quoted in Tables VI and VII. This selectivity is identical to that observed for hydrogen abstraction by chlorine atoms. By photochlorination of butane and isobutane with molecular chlorine at 40° in carbon tetrachloride a primary : secondary : tertiary selectivity of 1 : 2.5 : 3.2 was observed (see Part One page 60). Literature values for the

selectivity observed in chlorinations with molecular chlorine are:

for n-pentane and 2,3-dimethylbutane, 1 : 3.6 : 4.2 at 25° (16) and

for butane and isobutane, 1 : 3.5 : 4.8 at 40° in the vapor phase (48).

Relative reactivities obtained from competition experiments with sulfur monochloride and hydrocarbons were similar to relative reactivities observed for chlorinations with molecular chlorine (see Table IX). These results suggest that hydrogen abstraction is by chlorine atoms in the substitution reactions of sulfur monochloride with hydrocarbons.

The reaction of cyclohexylthiosulfenyl chloride (VI) with cyclohexane was studied to determine if it was the sole intermediate in the sulfur monochloride-cyclohexane reaction. From an examination of the product yields shown in Table X it was apparent that VI was not the only intermediate. First, VI did not give any detectable elemental sulfur in reactions with cyclohexane. Second, the yield of cyclohexyl chloride was lower, and the yield of dicyclohexyl disulfide was higher in reactions of VI with cyclohexane than in reactions of sulfur monochloride with cyclohexane. Because the product yields were not the same in both cases other intermediates must have been involved.

Müller and Schmidt (10) also noted that elemental sulfur was formed in the reactions which they studied and suggested that elemental sulfur results from formation of higher sulfur chlorides (ClS_xCl) which decompose to give elemental sulfur. The observation mentioned previously that reactions of VI with cyclohexane do not give any
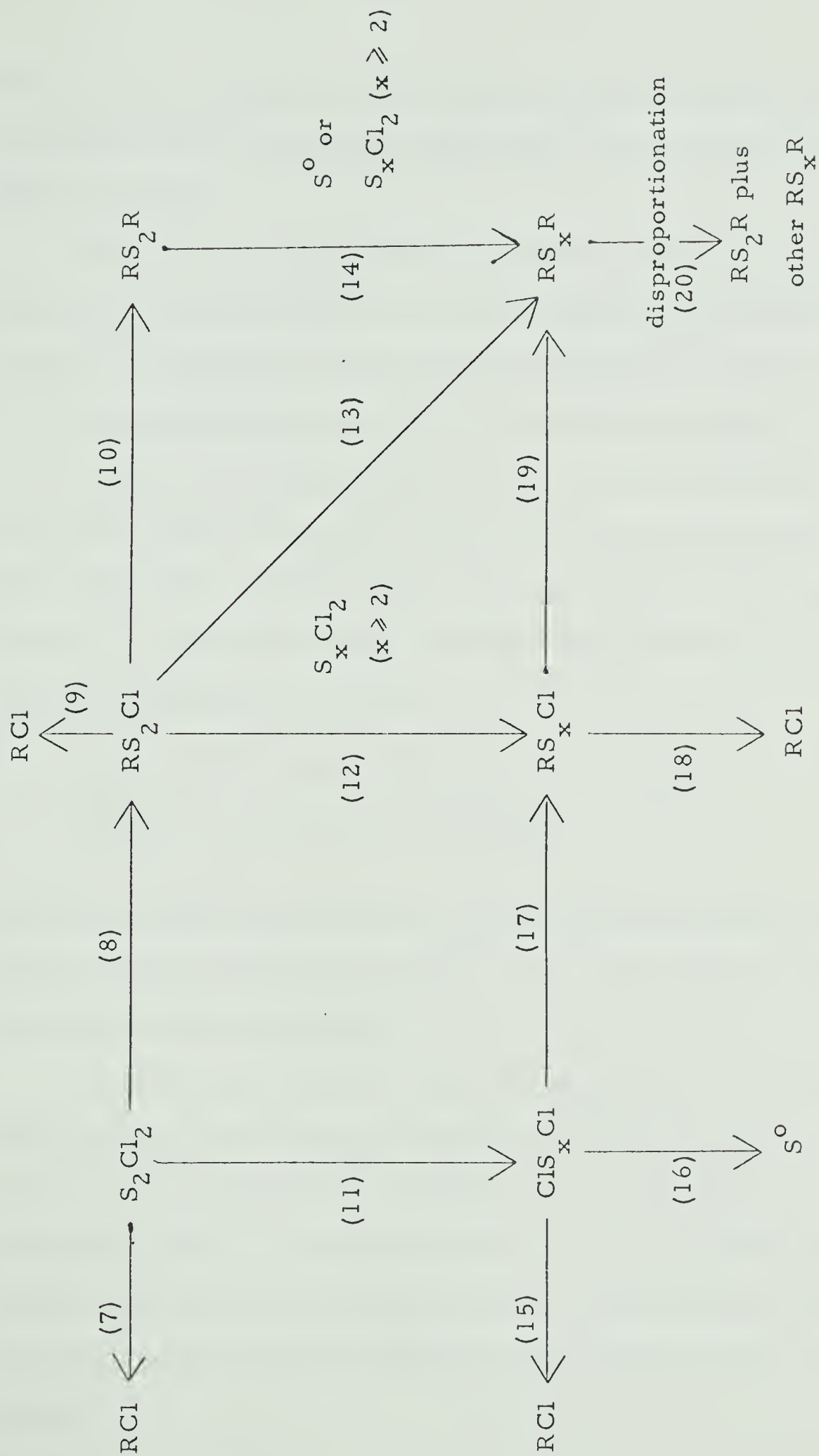
elemental sulfur constitutes good chemical evidence for the formation
of these higher sulfur chlorides as reaction intermediates. These
reactions are represented by equations 11 and 16 in Scheme I which
is an attempt to outline the transformations which occur in the
reaction of sulfur monochloride with hydrocarbons. The exact
nature of each of these transformations cannot be described because
of the indeterminacy of the chain nature of the reaction, i.e., the
transformations may involve either displacement or coupling reactions.

Equations 7, 9, 10 and 13 were included because the products
were observed reaction products in the photoinitiated reactions of
sulfur monochloride and VI with cyclohexane. Equations 15, 17, 18,
19 were included by analogy with equations 7, 8, 9 and 10 to take
into account the consequences of including the higher sulfur chlorides
as intermediates. It is plausible that these intermediates can under-
go transformation to alkyl chlorides and alkylpolythiosulfenyl chlorides
(RS_xCl). These latter compounds should in turn be able to give
dialkyl polysulfides (RS_xR).

Equations 12 and 14 were included in Scheme I on a tentative
basis because of results obtained by Grant and Van Wazer (51) for
related systems. The authors found that dialkyl disulfides incorpor-
ate sulfur to give polysulfides under conditions where radicals are
produced (heat or initiator). The authors also investigated the
condensation polymerization of sulfur dichloride and dimethyl sulfide
in which dimethyl disulfide and methylthiosulfenyl chloride were
intermediates. As equilibrium was obtained the concentrations of

SCHEME I

S^o or
S_xCl_2 $(x \geqslant 2)$

RS_2R

disproportionation
(20)

RS_xR

RS_2R plus

other RS_xR

(14)

(10)

(13)

(19)

RC1
(9)

RS_2Cl

S_xCl_2
$(x \geqslant 2)$

RS_xCl

RC1

(12)

(18)

(8)

(17)

S_2Cl_2

ClS_xCl

S^o

(11)

(16)

RC1
(7)

RC1
(15)

these two intermediates decreased with a concomitant increase in the concentrations of dimethyl polysulfides and methylpolythio-sulfenyl chlorides.

When VI was reacted with cyclohexane in the presence of elemental sulfur the yield of dicyclohexyl disulfide decreased while the yield of dicyclohexyl polysulfides remained the same (see Table X). The mechanistic reason for this result is not known.

Equation 20 was included to take into account the possibility that the polysulfides may have come from disproportionation of a single polysulfide. Tetrasulfides were considered in this connection because they could arise from alkylthiosulfenyl chlorides by the following sequence of reactions:

$$RS_2Cl \xrightarrow{\quad h\nu \quad} RS_2\cdot \quad + \quad Cl\cdot$$

$$2\ RS_2\cdot \xrightarrow{\qquad\qquad} RS_4R$$
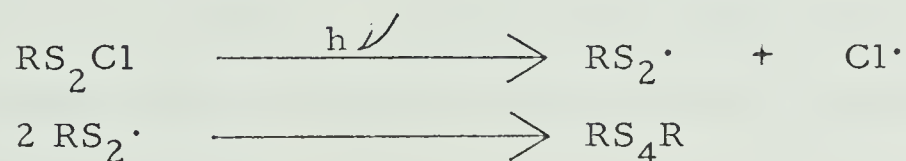
Pickering, Saunders and Tobolsky (52) found that dimethyl tetrasulfide undergoes disproportionation at 80° to give polysulfides ranging from the disulfide to the hexasulfide.

The importance of this reaction was checked first by determining the polysulfide composition from reaction of sulfur mono-chloride with isobutane (Table VIII) and then irradiating di-_t_-butyl tetrasulfide at 40°. The tetrasulfide was quite stable under these conditions (about 5% of disproportionation occurred after 150 hr), so disproportionation (equation 20) must assume only a minor role in Scheme I.

Scheme I predicts that the highest polysulfide which could result from reaction of an alkylthiosulfenyl chloride with a hydrocarbon is the tetrasulfide. Because higher polysulfides were produced in the sulfur monochloride-hydrocarbon reactions as seen from the reaction with isobutane as substrate, higher sulfur chlorides (ClS_xCl) and alkylpolythiosulfenyl chlorides (RS_xCl) were implicated as reaction intermediates. It was not possible to determine if dicyclohexyl tetrasulfide was the only polysulfide (in addition to the disulfide) in the reaction of VI with cyclohexane. A more satisfactory means of investigating this aspect of Scheme I would be to study the composition of the polysulfides resulting from reaction of t-butylthiosulfenyl chloride with isobutane using nuclear magnetic resonance as the means of analysis. If dialkyl tetrasulfides were the highest polysulfides obtained, then the above mentioned prediction of Scheme I would be verified.

The chemical evidence obtained in this study was not sufficient to enable the proposal of a reaction mechanism. The chief reasons for this were the indeterminacy of the chain nature of the reaction and the difficulties posed by the number of reaction intermediates probably involved. The nuclear magnetic resonance method developed by Grant and Van Wazer (51) allows the determination of individual dialkyl polysulfides and alkylpolythiosulfenyl chlorides (RS_xCl) for values of x from one to six if the resonance signal for the alkyl group is a singlet. With proper choice of substrate, application of this method to the study of reactions of sulfur monochloride with hydro-

carbons should enable a fuller understanding of the nature and inter-relation of the various reaction intermediates.
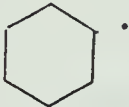
To complete the discussion two further points will be considered. The first is that in the sulfur monochloride-cyclohexane reaction the yield of hydrogen chloride (1.47 mole/mole of sulfur monochloride) exceeded the amount of cyclohexane which reacted (1.00 mole/mole of sulfur monochloride) suggesting extensive polysubstitution.   This large yield of hydrogen chloride must be related in part to the occurrence of the aromatic products cyclohexyl phenyl sulfide (IIIb) and o-chlorophenyl cyclohexyl sulfide (IV) obtained in very low yield. One explanation of these products is that initially dicyclohexyl sulfide, formed by reaction of alkyl radicals with dicyclohexyl di- or poly-sulfides, undergoes chlorination in the α-position or in both the α- and β-positions followed by successive elimination of hydrogen chloride and chlorination in the allylic position giving IIIb and IV. Since sulfides are known to readily undergo α-chlorination by an ionic mechanism (53), or α- and β-chlorination during photo-chlorination reactions with molecular chlorine (Part One, pages 61-62) there is some support for such an explanation.

Finally, the yields of alkyl chlorides and alkyl mercaptans can be used to calculate S values (previously described in Part One, page 39).   As used here, the S value for a given alkyl radical is the yield of alkyl mercaptan relative to the yield of alkyl chloride (RSH/RCl).   The S values for n-butyl, iso-butyl, sec-butyl, cyclohexyl, cyclopentyl and t-butyl radicals are summarized in Table XI.

TABLE XI

S VALUES FOR VARIOUS ALKYL RADICALS IN THE PHOTOINITIATED
REACTIONS OF SULFUR MONOCHLORIDE WITH HYDROCARBONS.

Radical	S Value[a] (RSH/RCl)
$CH_3CH_2CH_2CH_2\cdot$	2.9
	2.4
$CH_3CH_2\dot{C}HCH_3$	2.1
	2.1
	1.8
	1.3

[a] Defined in text.   All values for reactions carried out at 40°.

A small steric effect can be seen from examination of these S values

which decrease in going from a primary radical (2.9 for n-butyl) to a

secondary radical (2.1 for cyclohexyl) to a tertiary radical (1.3 for

t-butyl). This suggests that radical displacement reactions play at

least some part in the substitution reactions of sulfur monochloride

with hydrocarbons because this variation in S value might reflect

the differing ease of approach of an alkyl radical to the sulfur atom

of an S-Cl bond in a radical displacement reaction. The apparent

magnitude of this steric effect (S value decreases from 2.9 to 1.3 in

going from n-butyl to t-butyl) is much smaller than that observed for

pentachlorobenzenesulfenyl chloride (S value decreases from 40 to

2.5 in going from n-butyl to t-butyl). For this reason the steric

effect observed for sulfur monochloride cannot be taken to definitely

imply that radical displacement reactions are important.

Although these S values cannot be interpreted mechanistically

they can be used to predict the synthetic utility of sulfur monochloride

as a reagent for synthesizing mercaptans. These results predict

that mercaptan yields will be maximized when substitution occurs on

a primary carbon atom. Since other reagents such as sodium hydro-

sulfide employed in mercaptan syntheses react by ionic pathways (S_N2

substitution reactions on alkyl halides) good yields of primary

mercaptans can be obtained by the use of existing synthetic methods

(54). The neopentyl system seemed ideally suited as a system in

which to attempt a mercaptan synthesis because rearrangements can

accompany ionic displacement reactions in neopentyl systems, but

not in free-radical substitutions (55).

An existing synthesis reported in the literature (56) claims a

64% yield of neopentyl mercaptan from reaction of neopentyl p-tol- ·
uenesulfonate with sodium hydrosulfide, but no structural evidence
was offered to suggest that the mercaptan obtained was in fact
unrearranged material.

When sulfur monochloride was reacted with neopentane, a
46% yield of neopentyl mercaptan was isolated after reduction of the
polysulfides. The mercaptan possessed a nuclear magnetic reson-
ance spectrum consistent with an unrearranged neopentyl system.

Reaction of sulfur monochloride with adamantane and reduct-
ion of the polysulfides gave 1-adamantyl mercaptan and the previously
unreported 2-adamantyl mercaptan in 9% and 21% yield respectively.
The two isomers were obtained as a mixture which could be separated
by preparative gas liquid partition chromatography.

SUMMARY

Sulfur monochloride reacts with hydrocarbons by an inefficient
free-radical reaction to give alkyl chlorides and dialkyl polysulfides
in addition to hydrogen chloride and elemental sulfur. Cyclohexyl-
thiosulfenyl chloride reacts with cyclohexane to give the corresponding
products except that elemental sulfur is not a reaction product, and
the product distributions from the two reagents differ markedly,
demonstrating that cyclohexylthiosulfenyl chloride is not the sole
intermediate in the substitution reaction of sulfur monochloride with
cyclohexane. These results and the results of previous work in
related systems could be used to speculate about the nature of the

intermediates involved and their interrelation.   A mechanism could not be proposed for the reaction of sulfur monochloride with hydro-carbons because of the complexity of the system, but evidence from selectivities and relative reactivities suggests that hydrogen atom abstraction is by chlorine atoms.

The synthetic utility of sulfur monochloride as a reagent for synthesizing mercaptans was investigated with neopentane and adamantane.

EXPERIMENTAL

I.   MATERIALS AND REAGENTS.

REAGENTS

Sulfur monochloride and sulfur dichloride were supplied by Hooker Electrochemical Co. and were highest purity grade. Cyclohexene was Eastman white label. Dimethylamine was Matheson reagent grade gas. 2,4-Dinitrobenzenesulfenyl chloride was supplied by City Chemical Corp. and had m.p. 94-97°. Lithium aluminum hydride and calcium hydride were obtained from Metal Hydrides Inc..

HYDROCARBONS

Cyclohexane was Phillips Petroleum Co. pure grade material. Cyclopentane was Matheson, Coleman and Bell practical grade material. It was purified by treating with concentrated sulfuric acid, followed by dilute potassium permanganate solution. After drying and distillation it had b.p. 46.5° (700 mm) and was > 99.5% pure by glpc analysis. Butane, isobutane and neopentane were Phillips Petroleum Co. research grade gases. Toluene was purified by distilling from phosphorus pentoxide and had b.p. 107.5° (700 mm). Norbornane was supplied by Aldrich Chemical Co. and was sublimed before use. 2,3-Dimethylbutane was Phillips Petroleum Co. research grade. Adamantane was puriss grade material supplied by Aldrich Chemical Co..

REFERENCE COMPOUNDS AND STANDARDS

For peak enhancements in analyses by gas liquid partition chromatography (glpc) and nuclear magnetic resonance (nmr), reference compounds were reagent grade materials used as supplied. When used for glpc calibrations reference compounds were checked for purity (98% or better) and purified if required. The standards used for glpc analyses were found to be pure by that method. The Freon 112 (1,1-difluoro-1,2,2,2-tetrachloroethane) had b.p. 89.5-90.0° (700 mm); Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane) had b.p. 45.5° (704 mm). Standards used for nmr analyses were found to be pure by that method.

SOLVENTS AND MISCELLANEOUS MATERIALS

Skellysolve B and Skellysolve C were petroleum ether fractions b.p. 60-70° and 90-100° respectively. Carbon tetrachloride, chloroform, benzene, acetone, ethyl acetate and carbon disulfide were Shawinigan reagent grade solvents. Anhydrous ether was supplied by Mallinckrodt Chemical Works. Tetrahydrofuran (THF) was British Drug Houses reagent grade material. It was distilled from calcium hydride immediately before use to remove peroxides and water. The carbon tetrachloride solvent used in reactions of sulfur monochloride with hydrocarbons was Fisher Scientific Spectranalyzed Reagent. KEL-F oil was a polymer oil (KF-10) supplied by the Minnesota Mining and Manufacturing Co.

II.   METHODS AND PROCEDURES.

In general, the methods and procedures used were the same as those outlined in Part One of this thesis.

One additional instrument and several additional columns were used for glpc analyses.   All columns were constructed of stainless steel.

1.   Varian Aerograph Model A90-P3 with thermal conductivity

   detector.   The columns used were:

   a)   5' by 1/4" SE-30, 20% on 60/80 Chromsorb W

   b)   5' x 1/4" HALCOMID M 18 OL, 20% on 60/80 Chromsorb W.

2.   Varian Aerograph model 202.   The additional columns used were:

   a)   10' x 1/4" SE-30, 10% on 60/80 Chromsorb W AW

   b)   6' x 1/4" UCON POLAR, 10% on 60/80 Firebrick.

3.   Varian Aerograph model 600-D.   The additional columns used

   were:

   a)   10' x 1/8" SE-30, 5% on 80/100 Chromsorb W

   b)   10' x 1/8" SF-96, 5% on 80/100 Chromsorb W AW-DMCS.

For quantitation of alkyl chlorides and mercaptans by glpc, calibration data were obtained by analyzing at least three mixtures of known composition of standard and authentic material.

Spectral measurements were made on the same instruments. A Varian Associates HA-100 high resolution nmr spectrometer was used to obtain the 100 mc spectra.   Exact mass spectral measurements were made on the Associated Electronics Ltd. , MS9 instrument.

Analyses by thin-layer chromatography (tlc) were done on plates of Silica Gel GF 0.25 mm thick developed either by examining them under an ultraviolet (uv) light source or by placing them in an iodine chamber.

III.   SULFUR MONOCHLORIDE.

Sulfur monochloride was purified by the Method of Brauer (57). It was distilled from elemental sulfur (4% by weight) at atmospheric pressure b.p. 126° (680 mm), lit. (58) b.p. 135.6° . A further distillation from elemental sulfur (2% by weight) under reduced pressure gave pure material b.p. 71° (70 mm).

Anal. Calculated for S_2Cl_2: Cl, 52.51. Found: Cl, 52.39, 52.45.

The uv spectrum (C_6H_{12}) showed maxima at 201 (log ϵ 3.71) and 265 mμ (log ϵ 3.83). Literature values (10, 59) are 265 and 266 mμ (log ϵ 3.80). The absorbance went to zero above 510 mμ for a concentrated solution (1.1 x 10^{-2} M). For 1% of contaminating sulfur dichloride the absorbance would have been 0.01 at 520 mμ (59). This absence of absorption above 510 mμ, the excellent agreement of the extinction coefficient at 265 mμ with the literature value (59) and the elemental analysis were taken as proof of the absence of sulfur dichloride in the purified sulfur monochloride.

After purification the sulfur monochloride was stored at room temperature protected from light and atmospheric moisture.

For determination of active chlorine carbon tetrachloride

solutions of sulfur monochloride were stirred one hr with excess

potassium iodide in 10% aqueous acetic acid.   The iodine liberated

was titrated with 0.1 M standard aqueous sodium thiosulfate solution.

S_2Cl_2, g	ml of 0.1000 M $Na_2S_2O_3$	
	found	required
0.1202	17.72	17.82
0.0973	14.28	14.42

The stoichiometry used in calculating the theroretical titer

was:

$$S_2Cl_2 \;+\; 2\,KI \longrightarrow S^{o} + 2\,KCl \;+\; I_2$$
$$2\,S_2O_3^{=} + I_2 \longrightarrow S_4O_6^{=} + 2\,I^{-}$$
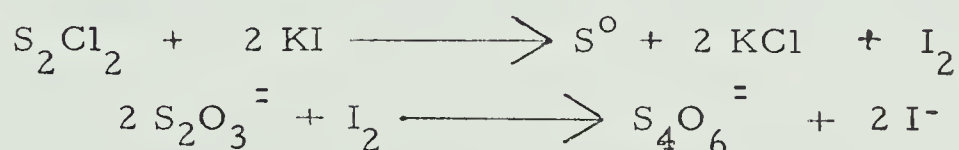
IV.   REACTIONS OF SULFUR MONOCHLORIDE WITH CYCLO-
       HEXANE.

GENERAL PROCEDURE

Standard solutions of sulfur monochloride (usually 0.3 M) and

cyclohexane (usually 3 M) were prepared with carbon tetrachloride

solvent.   Aliquots were pipetted into Pyrex ampoules which were

degassed and sealed under vacuum.   After equilibration in a Pyrex

water bath at 40.0 ± 0.1^{o}, the ampoules were irradiated with two

200 w tungsten lamps placed at a distance of 3-4 inches.   Irradiation

times were 20-80 hr depending on the size of sample and initial

concentration of reactants.   The reactions could be followed visually.

After several hr, the original pale yellow color of the sulfur mono-
chloride had deepened. As the reactions progressed this yellow
color faded until, at complete reaction, the reaction mixtures were
nearly colorless. Several reaction mixtures were tested at this
point with moist potassium iodide-starch paper and found to be free
from active chlorine.

QUALITATIVE PRODUCT ANALYSIS

When reaction ampoules were opened the sharp smell of
hydrogen chloride was apparent. When the escaping gas was bubbled
through water, the aqueous portion acidified and silver nitrate solution
added, a small amount of white silver chloride precipitate was
observed.

The absence of hydrogen sulfide was indicated by the following
test. An ampoule was broken open under a small volume (20 ml) of
water. After vigorous shaking the aqueous portion was acidified with
acetic acid and lead acetate solution added. No black precipitate of
lead sulfide was observed.

Removal of the solvent from reaction mixtures left a pale
yellow oily residue from which a solid slowly crystallized. This
solid was isolated and was identical to elemental sulfur in melting
point ($116-118^{\circ}$), mixture melting point, R_f upon analysis by tlc on
silica gel, and color test with pyridine-sodium hydroxide reagent (60).

The solvent was removed at 30° from 80 ml of product solution
(4 x 20 ml originally 0.296 M in sulfur monochloride and 2.8 M in
cyclohexane). The residue was then heated on a steam bath in a flask

connected to a small cold trap which was in turn connected to a water aspirator and cooled in dry ice. In this way, crude cyclohexyl chloride (I) containing carbon tetrachloride and cyclohexane was distilled. Distillation in a short path apparatus gave 0.3 g of a colorless liquid b.p. > 120° (705 mm), n_D^{20} 1.464. Lit. (61) n_D^{20} 1.462 for cyclohexyl chloride. The IR spectrum (CCl_4) was identical to that of authentic cyclohexyl chloride.

The product solutions from reactions run at the usual concentrations were too dilute to enable effective glpc analysis. For qualitative analysis a product solution was concentrated by fractional distillation and then analyzed by glpc (model A90-P3, 5' SE-30 column programmed from 100-220°, 60 ml He/min). The glpc chromatogram showed a complex mixture of products. Cyclohexyl chloride (I) appeared first in the chromatogram and was the major component. It was identified by retention time comparison. Following it was a small amount (< 1%) of cyclohexyl mercaptan (II), identified by retention time comparison. Next was a series of eight very minor components presumed to be di- and polychlorinated cyclohexanes. The next component (III) had the same retention time as dicyclohexyl sulfide. It was followed by two more components IV and V. Component V possessed the same retention time as dicyclohexyl disulfide. For further identification III, IV and V were collected by preparative glpc.

When III was compared with dicyclohexyl sulfide by tlc the following observation was made. Authentic dicyclohexyl sulfide could

not be observed on the tlc plates under ultraviolet irradiation, but

detection could be accomplished by spraying with phosphomolybdic

acid. Compound III could be observed under ultraviolet irradiation.

It also moved as a single compound possessing the same R_f as dicyclo-

hexyl sulfide. This indicated that III was a mixture of dicyclohexyl

sulfide and at least one other component. The mass spectrum of III

showed parent ions at m/e 198 ($C_{12}H_{22}S$ = 198) and m/e 192 ($C_{12}H_{16}S$

= 192). From this information it was reasoned that III was most

likely a mixture of dicyclohexyl sulfide (IIIa) and phenyl cyclohexyl

sulfide (IIIb).

A sufficient amount of IV was collected to obtain mass, IR and

uv spectral data. The mass spectrum had parent peaks at m/e 226

and 228 in the ratio 3 : 1, the proper ratio for ^{35}Cl and ^{37}Cl. The

base peaks were at m/e 144 and 146 again in the ratio 3 : 1. An

exact mass determination on the parent ion at m/e 226 gave the

molecular formula. Calculated for $C_{12}H_{15}^{35}ClS$; m/e 226.0583.

Found; m/e 226.0581. For the neat liquid the IR bands were at

3055 (aromatic C-H), 2930, 2850, 1450, 1435 (aliphatic C-H), 1580,

1565 (aromatic C≡C) and 750 cm^{-1} (1,2-disubstituted benzene or C-Cl).

The ultraviolet maxima for a 10^{-4} M solution of IV in cyclohexane

were at 206 (log ϵ 4.2), 215 (log ϵ 4.1), 233 (log ϵ 4.1), 258 (log ϵ

3.8, with a shoulder at 262), 286 (log ϵ 3.5), 300 (log ϵ 3.0) and 326

mμ (log ϵ 2.6). By consulting spectral data for model compounds

(62) the maxima predicted for o-, m- and p-chlorophenyl cyclohexyl

sulfide were 257, 262 and 264 mμ respectively. The structure which

best explained the spectral data was o-chlorophenyl cyclohexyl

sulfide. It was possible that IV also contained small amounts of the

m- and p- isomers because the presence of these isomers could not

be discounted on the basis of the spectral data obtained.

Compound V was identical to authentic dicyclohexyl disulfide

with respect to R_f by tlc, mass spectrum and IR spectrum.

SYNTHESIS OF DICYCLOHEXYL DISULFIDE

Cyclohexyl mercaptan (5.80 g, 0.05 mole), 30% hydrogen

peroxide (3.3 ml, 1 g H_2O_2, 0.03 mole), a few drops of 3 M hydro-

chloric acid, and 40 ml of ethanol were stirred at 60-70° for 5 hr.

The reaction mixture was poured onto ice and ether extracted (2 x 50

ml). The ether extracts were washed with sodium bisulfite solution,

sodium bicarbonate solution and water, then dried over magnesium

sulfate. Removal of the solvent and distillation of the residue under

reduced pressure gave 1.7 g (30%) of dicyclohexyl disulfide as a

colorless oil b.p. 151-155° (1.2 mm), n_D^{25} 1.5456. Lit. (63) b.p.

166-168° (8 mm), n_D^{20} 1.5476.

SYNTHESIS OF DICYCLOHEXYL SULFIDE

Cyclohexyl mercaptan (4.64 g, 0.04 mole), cyclohexene (4.50

ml, 3.64 g, 0.0044 mole) and azobisisobutyronitrile (0.040 g, 0.00024

mole) were heated to reflux in 50 ml of carbon tetrachloride. After

27 and 37 hr further 0.020 g portions of initiator were added. After

66 hr the reaction was stopped, the solvent removed and the residue

distilled under reduced pressure. After a low boiling forerun was

collected, a total of 1.5 g (19%) of product was collected in two fractions: fraction 1 b.p. 137-143° (20 mm), n_D^{26} 1.5122; fraction 2 b.p. 143-149° (20 mm), n_D^{26} 1.5150 [lit. (63) b.p. 136-138° (8 mm), n_D^{20} 1.5146; (64) b.p. 140-144° (13 mm), n_D^{20} 1.5143] .

SYNTHESIS OF CYCLOHEXYL 2,4-DINITROPHENYL DISULFIDE

Cyclohexyl mercaptan (1.16 g, 0.01 mole) and 2,4-dinitro-benzenesulfenyl chloride (2.34 g, 0.01 mole) in 25 ml of carbon tetrachloride were heated on a steam bath for 0.25 hr. After cooling, the solvent was removed and the crude product crystallized from ethanol. Yield of yellow needles was 1.8 g (58%) m.p. 115-116°; IR (CCl$_4$) 1590, 1515 (aromatic C=C), 1340 (aromatic -NO$_2$) and 885, 830 cm^{-1} (1,2,4-trisubstituted benzene); nmr (CDCl$_3$) τ 0.9 (d, 1), τ 1.45 (d, 2), τ 6.7-7.5 (m, 1) and τ 7.6-9.2 (m, 10). An analytical sample was prepared by recrystallizing a sample twice from chloroform-Skellysolve B m.p. 115.5-116.5°.

Anal. Calculated for C$_{12}$H$_{14}$N$_2$O$_4$S$_2$: C, 45.84; H, 4.49; N, 8.91. Found: C, 45.57; H, 4.57; N, 9.00.

ISOLATION OF CYCLOHEXYL 2,4-DINITROPHENYL DISULFIDE AFTER REDUCTION OF A POLYSULFIDE MIXTURE WITH LITHIUM ALUMINUM HYDRIDE

Four 20 ml portions of sulfur monochloride (0.111 M, 0.009 mole) and cyclohexane (2.8 M, 0.22 mole) in carbon tetrachloride were irradiated at 40° until the reaction was completed. The solvent and excess hydrocarbon were removed from the combined

reaction mixtures. Elemental sulfur was removed by column

chromatography as described in the next section (Quantitative Pro-

duct Analysis).

The polysulfide fractions (0.66 g) eluted with Skellysolve B-

chloroform and chloroform were dissolved in ether (50 ml) and added

to lithium aluminum hydride (1.00 g) in 75 ml of ether at 0°. The

reaction mixture was stirred at room temperature for 4 hr and heated

under reflux for 20 hr. After cooling to 0°, excess hydride was

decomposed by dropwise addition of water. The ether solution was

filtered, dried over anhydrous sodium sulfate and concentrated by

distillation through a short Vigreux column. To the residue was

added 2,4-dinitrobenzenesulfenyl chloride (0.47 g, 2.0 mmole) and

ethanol-free chloroform (25 ml). The mixture was heated to reflux

for 0.5 hr and then the solvent was removed. Crystallization of the

residue from ethanol gave 0.35 g of yellow needles m.p. 100-110°,

and a second crystallization from ethanol gave 0.25 g m.p. 100-112°.

Pure cyclohexyl 2,4-dinitrophenyl disulfide was obtained by chromato-

graphy on 10 g of silica gel. The material eluted with carbon tetra-

chloride-chloroform (3 : 1, v/v) weighed 0.17 g (0.54 mmole) and had

m.p. 114.5-115.5°. The mixture m.p. with authentic material was

undepressed and the IR spectrum (CCl_4) and nmr spectrum ($CDCl_3$)

were identical to those of authentic material.

QUANTITATIVE PRODUCT ANALYSIS

Hydrogen chloride yields for the sulfur monochloride-cyclo-

hexane reactions were determined by breaking ampoules under 50-100

ml of water in a stoppered flask, shaking the flask for 10-15 min
and titrating the hydrogen chloride with standard 0.1M sodium
hydroxide solution using phenolphthalein as the indicator. The
concentrations of reactants and yields of hydrogen chloride are
summarized in Table II.

Elemental sulfur could conveniently be isolated from the
reaction mixtures by column chromatography. Four reaction
mixtures (20 ml each) from sulfur monochloride (0.111 M, 0.009
mole) and cyclohexane (2.8 M, 0.22 mole) were combined and
evaporated. Treatment of the residue with Skellysolve B left 0.097 g
of undissolved elemental sulfur. Chromatography of the soluble
portion on silica gel (70 g) gave a further 0.104 g of elemental sulfur
eluted with Skellysolve B. The total yield of sulfur (0.201 g)
represented 35% of the sulfur originally present as sulfur mono-
chloride. The sulfur isolated was identified by m.p., mixture m.p.
with authentic material and R_f upon analysis by tlc. In a second
experiment using two 10 ml portions of sulfur monochloride (0.30 M,
0.006 mole) and cyclohexane (3.0 M, 0.06 mole) in carbon tetrachloride
a total of 0.114 g of sulfur was isolated after analysis of the reaction
mixtures. This represented 30% of the sulfur originally present as
sulfur monochloride.

Cyclohexyl chloride was determined by analyzing reaction
mixtures by glpc (model A90-P3, 5' SE-30 at 100°, 30 ml He/min)
after addition of chlorobenzene as the external standard. The order
of elution was cyclohexane-carbon tetrachloride, chlorobenzene and

cyclohexyl chloride. The concentrations of reactants and yields of cyclohexyl chloride are summarized in Table III.

Dicyclohexyl disulfide was estimated for one reaction mixture (sulfur monochloride 0.31 M, cyclohexane 3 M in carbon tetrachloride) by glpc (model A90-P3, 5' SE-30 programmed from 115-200°) after addition of naphthalene as the external standard. A yield of 0.084 mole of dicyclohexyl disulfide / mole of sulfur monochloride was determined.

Analysis by glpc of a representative reaction mixture allowed an estimate of the yields of III, IV and V to be made by comparison of peak areas with cyclohexyl chloride. The yields estimated in this way as mole/mole of sulfur monochloride were: III, 0.005; IV, 0.01; V, 0.077.

QUANTITATION OF DICYCLOHEXYL POLYSULFIDES BY NUCLEAR MAGNETIC RESONANCE

A 10 ml portion of a reaction mixture (sulfur monochloride 0.306 M, cyclohexane 3.0 M in carbon tetrachloride) was evaporated and benzyl chloride (0.062 g, 0.49 mmole) was added to the residue. From the nmr spectrum (benzene) the ratio of the methylene protons of the standard (τ 5.9) to the α-protons of the dicyclohexyl poly-sulfides (τ 6.7-7.7) was 1 : 1.9. From this, a yield of 0.30 mole of dicyclohexyl polysulfides (including the disulfide) per mole of sulfur monochloride was calculated. Resonances for the α-proton of residual cyclohexyl chloride and the ring protons were observed at τ 6.1-6.5 and τ 7.7-9.4.

QUANTITATION OF DICYCLOHEXYL POLYSULFIDES BY REDUCT-
ION TO CYCLOHEXYL MERCAPTAN WITH LITHIUM ALUMINUM
HYDRIDE

Preliminary experiments using zinc in aqueous acetic acid-
sulfuric acid as the reducing agent gave unsatisfactory results
because of the unreproducible yields obtained.

Arnold, Lien and Alm (65) found that lithium aluminum hydride
in boiling tetrahydrofuran (THF) was an effective reagent for the
reduction of dialkyl di- and trisulfides to alkyl mercaptans. Based
on this a method was developed for reducing polysulfides and thereby
quantitating them as the mercaptan(s).

Two reaction mixtures [5.00 ml of a carbon tetrachloride
solution of sulfur monochloride (0.316 M, 1.58 mmole) and cyclo-
hexane (3.1 M, 15.5 mmole)] were evaporated and the residues
reduced and analyzed by the following procedure.

The residue in THF (5 ml) was added dropwise with stirring
to lithium aluminum hydride (0.20 g) in THF (10-20 ml) at 0°. The
reaction mixture was stirred at room temperature for 0.5 hr and
then heated under reflux for 3 hr. Excess hydride was decomposed
by dropwise addition of water to the cooled solution (0°). Toluene
was added as the standard by pipetting a standard solution of toluene
in THF into the reaction mixture. After addition of concentrated
hydrochloric acid (2 ml) and stirring for 10-15 min the reaction
mixture was analyzed for cyclohexyl mercaptan by glpc (model 600-D,
10' SE-30 programmed from 40-150°). The order of elution was

THF, toluene and cyclohexyl mercaptan. The yield of cyclohexyl mercaptan was 0.608 ± 0.020 mole/mole of sulfur monochloride for the two reactions analyzed. By addition of thiophenol to the mixture after reduction and reanalysis by glpc it was shown that thiophenol was absent as a product (after reduction).

CYCLOHEXANE CONSUMPTION

Cyclohexane consumption was determined by preparing solutions of carbon tetrachloride, cyclohexane and sulfur monochloride by weight so that the molar concentration of each component was accurately known. After completion of reaction glpc analysis (model A90-P3, 5' HALCOMID M 18 OL at 40°, 40 ml He/min; or model 202, 6' UCON POLAR at 55°, 40 ml He/min) of the reaction mixtures provided the peak area ratio of carbon tetrachloride to cyclohexane. From calibration curves this peak area ratio was converted to a molar ratio, and assuming that no carbon tetrachloride was consumed, the final molar concentration of cyclohexane was thus determined. From this, the moles of cyclohexane consumed per mole of sulfur monochloride reacting could be calculated. The results are summarized in Table IV.

V. REACTION OF SULFUR MONOCHLORIDE WITH CYCLOPENTANE.

SYNTHETIC REACTION: CYCLOPENTYL MERCAPTAN

Cyclopentane (125 ml, 94 g, 1.3 mole) and sulfur monochloride (16.8 g, 0.125 mole) were placed in a three-neck flask equipped with a magnetic stirrer and reflux condenser. The condenser outlet was

connected to a gas bubbler filled with KEL-F oil so that a positive pressure was maintained in the reaction vessel. After flushing the system with nitrogen, irradiation was begun with two 200 w incandescent lamps at a distance of about 3 inches from the reaction vessel. The heat from the lamps caused a gentle reflux of the cyclopentane. After 5 days, iodometric titration of an aliquot of the reaction mixture showed that 25% of the active chlorine still remained. The deep amber reaction mixture was stirred with excess potassium iodide in 10% aqueous acetic acid. The aqueous portion was separated and the organic layer was washed with aqueous sodium thiosulfate solution (2 x) and water (2 x), then dried over anhydrous sodium sulfate. Most of the excess cyclopentane was removed by distillation. Crude cyclopentyl chloride was isolated from the mixture by the method previously described for isolation of cyclohexyl chloride. There was obtained 1.2 ml (ca. 1 g) of material consisting of cyclopentane (40%) and cyclopentyl chloride (60%) as determined by glpc analysis (model A90-P3, 5' SE-30 at 100°). Pure material was obtained by preparative glpc, n_D^{20} 1.4504, lit. (61) n_D^{20} 1.451. It possessed nmr (CCl_4) and IR (CCl_4) spectra identical to authentic material.

The polysulfides remaining after isolation of the cyclopentyl chloride were reduced with lithium aluminum hydride (6 g, 0.16 mole) in THF (100 ml) by the method previously described. The product was isolated by pouring the reaction mixture into 300 ml of ice-water containing 30 ml of sulfuric acid, extracting with Skellysolve B

(2 x 250 ml), washing the combined extracts with water (3 x 200 ml), removal of dark colored impurities by passing through a short column of alumina, removal of the solvent and distillation of the residue. There was obtained 2.3 g (18%) of cyclopentyl mercaptan b.p. 127-128° (700 mm), lit. (63) b.p. 129.5-130.5° (748 mm); nmr (CCl$_4$) τ 6.6-7.1 (m, 1, S – C – H), τ 7.7-8.8 (m, 8, ring protons) and τ 8.6 (d, 1, J = 5.5 cps, S-H). Analysis by glpc showed it to contain 5% of an impurity. Pure material was obtained by preparative glpc (model A90-P3, 5' SE-30 at 100°); IR (CCl$_4$) 2960, 2910, 2870, 1445 (C-H) and 2575 cm^{-1} (S-H). The S-H absorption could only be observed for concentrated solutions (10-20%). This purified material was used for the glpc calibration in the subsequent quantitative work.

QUANTITATIVE ANALYSIS OF SULFUR MONOCHLORIDE-CYCLO-PENTANE REACTIONS FOR CYCLOPENTYL CHLORIDE AND DICYCLOPENTYL POLYSULFIDE YIELDS

Three degassed portions (5.00 ml) of sulfur monochloride (0.303 M, 1.52 mmole), cyclopentane (3.4 M, 17 mmole) and Freon 112 (0.209 M, 1.04 mmole, internal standard) in carbon tetrachloride were irradiated for 46 hr at 40°.

The ampoules were frozen in liquid nitrogen and broken open in a stoppered flask containing potassium iodide (1 g) and water (50 ml). After iodometric titration for active chlorine potassium iodate (0.5 g) was added and hydrogen chloride was titrated iodometrically.

$$5 \ KI + KIO_3 + 6 \ H^+ \longrightarrow 3 \ H_2O + 6 \ K^+ + 3 \ I_2$$
$$2 \ S_2O_3^= + I_2 \longrightarrow S_4O_6^= + 2 \ I^-$$

After this titration, small aliquots of the organic layer were removed and analyzed for cyclopentyl chloride by glpc (model 600-D, 10' SF-96 at 60°). The order of elution was cyclopentane, carbon tetrachloride, Freon 112 and cyclopentyl chloride. Molar yields were calculated in the usual manner by comparing peak area ratios of Freon 112 and cyclopentyl chloride.

The organic portion remaining in the flask after titration was separated quantitatively from the aqueous portion, washed once with water and passed through a short column of silica gel to remove traces of water. The solvent was removed and the residues analyzed for polysulfide yields.

One reaction mixture was analyzed by nmr using 1,3,5-tri-bromobenzene as the standard in a method analogous to that used previously in analyzing for dicyclohexyl polysulfides. In this way a yield of 0.38 mole of dicyclopentyl polysulfide/mole of sulfur mono-chloride was found. The two remaining polysulfide residues were reduced by the method previously described (lithium aluminum hydride in THF). Cyclopentyl mercaptan was determined by glpc (model 600-D, 10' SE-30 programmed from $40-150^o$) using toluene as the standard. The order of elution was THF, toluene and cyclopentyl mercaptan.

The product yields are summarized in Table V.

VI.   REACTION OF SULFUR MONOCHLORIDE WITH BUTANE.

GENERAL PROCEDURE

The desired amount of hydrocarbon (5 ml, 50 mmole) was transferred into an ampoule cooled in dry ice and premeasured for the required volume.   An aliquot (10.0 ml) of a standard solution of sulfur monochloride (0.3 M, 3.0 mmole) and Freon 112 (0.2 M, 2.0 mmole) in carbon tetrachloride was then pipetted into the ampoule. The ampoule was degassed, sealed under vacuum and irradiated at 40° for 80-100 hr.   Formation of insoluble, colored material was apparent in the later stages of reaction.

The Freon 112 was omitted from reaction mixtures used for qualitative product analysis.

QUALITATIVE PRODUCT ANALYSIS

The primary and secondary alkyl chlorides were identified by glpc retention time comparison on two columns (model 600-D, 20' SF-96 and 25' UCON POLAR columns both at 50°).   The order of elution was butane, sec-butyl chloride, n-butyl chloride and carbon tetrachloride.   Analysis of the high boiling products by glpc (model 600-D, 20' SF-96 column programmed from 50-200°) showed a complex pattern of 10-15 peaks in the chromatogram.   This pattern was dependent on the injector temperature, indicative of decomposition. Because of this complexity, structural information was sought from IR and nmr spectra, and by reducing the polysulfides to the mercaptans with lithium aluminum hydride.

The IR spectrum of the products remaining after removal of alkyl chlorides and solvent had characteristic bands for C-H at 2960, 2925, 2870, 1460, 1380 and 1345 cm^{-1}. The region 1600-1700 cm^{-1} was free of absorption due to $C=C$ stretching.

A reaction was carried out on a small scale in a sealed Pyrex nmr tube using the same proportions of reactants and solvent as before. Scanning the region τ 2-6 at high sensitivity failed to reveal the presence of any olefinic protons.

LITHIUM ALUMINUM HYDRIDE REDUCTION OF POLYSULFIDES: IDENTIFICATION OF n-BUTYL AND sec-BUTYL MERCAPTANS AS THEIR 2,4-DINITROBENZENESULFENYL DERIVATIVES

The polysulfides from reaction of sulfur monochloride (2.9 mmole) with excess butane (50 mmole) were reduced with lithium aluminum hydride (0.30 g, 8 mmole) in ether (50 ml, heated to reflux for 24 hr). After reduction and decomposition of excess hydride the ether solution was dried over anhydrous sodium sulfate and then treated with 2,4-dinitrobenzenesulfenyl chloride (0.25 g, 1.1 mmole) for 3 hr at room temperature. Removal of the solvent left 0.25 g of a yellow oil (VII) which could not be crystallized even after chromatography on silica gel. The nmr spectrum $(CDCl_3)$ of VII was identical to that of a 40 : 60 mixture of n-butyl 2,4-dinitrophenyl disulfide (VIII) and sec-butyl 2,4-dinitrophenyl disulfide (IX). The mixture (VII) moved as a single compound when subjected to analysis by tlc $(CHCl_3)$. The R_f of VII was identical to that of VIII and IX.

SYNTHESIS OF n-BUTYL 2,4-DINITROPHENYL DISULFIDE (VIII) AND sec-BUTYL 2,4-DINITROPHENYL DISULFIDE (IX)

The derivatives were prepared from the mercaptans (5-7 mmole) and an equivalent amount of 2,4-dinitrobenzenesulfenyl chloride by the usual method (66).

n-Butyl 2,4-dinitrophenyl disulfide (VIII) was obtained in 57% yield and had m.p. 45-46° (methanol), [lit. (66) m.p. 44-45°, (67) m.p. 46-47°]; nmr (CDCl$_3$) τ 1.10 (t, 1, aromatic H$_3$), τ 1.64 (d, 2, aromatic H$_5$ and H$_6$), τ 7.22 (t, 2, J = 6.7 cps, -S-CH$_2$-), τ 8.0-8.9 (m, 4, -CH$_2$CH$_2$-) and τ 8.9-9.3 (m, 3, -CH$_3$).

sec-Butyl 2,4-dinitrophenyl disulfide (IX) was obtained in 73% yield and had m.p. 58-59° (methanol); nmr (CDCl$_3$) τ 1.11 (t, 1, aromatic H$_3$), τ 1.64 (q, 2, aromatic H$_5$ and H$_6$), τ 7.10 (sextet, 1, J = 6.5 cps, -S-$\overset{|}{\underset{|}{C}}$-H), τ 8.0-8.8 (m, 2, -CH$_2$-), τ 8.68 (d, 3, J = 6.5 cps, -CH$_3$) and τ 8.97 (t, 3, J = 6.8 cps, -CH$_3$). An analytical sample of IX prepared by two recrystallizations from methanol had m.p. 58.5-59.5°.

Anal. Calculated for C$_{10}$H$_{12}$N$_2$O$_4$S$_2$: C, 41.65; H, 4.20; N, 9.72. Found: C, 41.49; H, 4.16; N, 9.66.

QUANTITATIVE PRODUCT ANALYSIS

Reactions were carried out as described under General Procedure. The ampoule containing the reaction mixture was frozen in liquid nitrogen, opened and analyzed by glpc (model 600-D, 20' SF-96 at 50°) for n-butyl and sec-butyl chloride. Molar yields were calculated by using Freon 112 as the internal standard and are

summarized in Table VI. After analysis the contents of the ampoule were transferred to a flask and stirred with potassium iodide in 10% aqueous acetic acid in order to determine the active chlorine remaining by iodometric titration. After the titration the organic layer was transferred quantitatively to a separatory funnel, washed once with water and passed through a small column of silica gel to remove traces of water and acetic acid. The solvent was removed and the polysulfide residue was analyzed by either nmr or reduction with lithium aluminum hydride.

1. Nuclear Magnetic Resonance Method

A known amount of anisole was added as a standard to the polysulfide residue and the nmr spectrum of the mixture was obtained using carbon tetrachloride as the solvent. In preparing the samples undissolved elemental sulfur was removed by filtration. The spectrum was assigned by comparison with di-n-butyl and di-sec-butyl disulfides as model compounds by peak enhancement. Terminal methyl groups appeared as overlapping signals at τ 8.8-9.3, the doublet for the -S-CH-CH$_3$ methyl group was at τ 8.63, methylene protons were from τ 8.0-8.8, and the α-protons were unresolved from τ 6.8-7.6 in good agreement with literature values (68) for the chemical shifts of the α-protons of di-n-butyl and di-sec-butyl di-, tri- and tetra-sulfides. The isomer ratios could be estimated in the following way. If the mole fraction of n-butyl groups was set equal to x, and the mole fraction of sec-butyl groups was set equal to y, then x + y = 1.00.

The relationship,

$$x = \frac{A}{B} - 1.00$$

where A was the integration for all of the α-protons and B was the integration for one proton gave x and thereby gave y. The total mmoles of alkyl groups was calculated by comparing their nine proton integration to the eight proton integration of the standard (anisole), thus giving the absolute mmolar yields of n-butyl groups and sec-butyl groups. The results are summarized in Table VI.

2. Lithium Aluminum Hydride Reduction Method

The polysulfide residue was reduced with lithium aluminum hydride (0.25 g) in THF (15 ml, heated to reflux for 3 hr) by the method previously described. Freon 113 was added as the external standard for glpc analysis of n-butyl and sec-butyl mercaptans (model 600-D, 20' SF-96 at 50°). The order of elution was Freon 113, THF, sec-butyl mercaptan and n-butyl mercaptan. The mercaptans were compared to authentic materials with respect to retention time and were found to be identical to them in this respect. The mercaptan yields are presented in Table VI.

VII. REACTION OF SULFUR MONOCHLORIDE WITH ISOBUTANE.

GENERAL PROCEDURE

The procedure and concentrations of reactants and solvent were the same as those used for the sulfur monochloride-butane reactions. Shorter irradiation times (40-60 hr) were required. Completeness

of reaction was shown by a negative test for active chlorine with potassium iodide-starch paper.

QUALITATIVE PRODUCT ANALYSIS

iso-Butyl and t-butyl chloride were identified in the reaction mixtures by comparison of glpc retention times on two columns (model 600-D, 20' SF-96 and 25' UCON POLAR both at 50°). The order of elution was isobutane, iso-butyl chloride, t-butyl chloride and carbon tetrachloride.

Again, as with the butane reaction mixtures, the qualitative analysis of the polysulfides was by IR and reduction techniques.

The IR spectrum of the residue remaining after removal of alkyl chlorides and solvent had absorption bands for C-H at 2950, 2920, 2890, 2860, 1460, 1385 and 1365 cm^{-1}, a weak band at 1660 cm^{-1} (C$=$C trisubstituted) and a weak band at 1730 cm^{-1} (C$=$O). The origin of the carbonyl band was unknown.

LITHIUM ALUMINUM HYDRIDE REDUCTION OF POLYSULFIDES: IDENTIFICATION OF iso-BUTYL AND t-BUTYL MERCAPTANS AS THEIR 2,4-DINITROBENZENESULFENYL DERIVATIVES

The polysulfides from reaction of sulfur monochloride (3.0 mmole) with isobutane (50 mmole) were reduced with lithium aluminum hydride (0.30 g, 8 mmole) in ether (50 ml, heated to reflux for 24 hr). The 2,4-dinitrobenzenesulfenyl derivatives were prepared from the ether solution of mercaptans and 2,4-dinitrobenzenesulfenyl chloride (0.25 g, 1.1 mmole). Removal of the ether and crystallization of the

residue from methanol gave 0.19 g of yellow needles m.p. 82-90°.

The nmr spectrum of this solid was identical to that of an 85 : 15

mixture of iso-butyl 2,4-dinitrophenyl disulfide (X) and t-butyl 2,4-

dinitrophenyl disulfide (XI). The mixture could not be resolved

by tlc but had R$_f$ identical to X and XI.

SYNTHESIS OF iso-BUTYL 2,4-DINITROPHENYL DISULFIDE (X) AND t-BUTYL 2,4-DINITROPHENYL DISULFIDE (XI)

The derivatives were prepared by the usual method (66) from

the mercaptans (5-7 mmole) and an equivalent amount of 2,4-dinitro-

benzenesulfenyl chloride.

iso-Butyl 2,4-dinitrophenyl disulfide was obtained in 71%

yield m.p. 92.5-93.5° (methanol); nmr (CDCl$_3$) τ 1.09 (d, 1,

aromatic H$_3$), τ 1.64 (d, 2, aromatic H$_5$ and H$_6$), τ 7.33 (d, 2,

J = 6.5 cps, -S-CH$_2$-), τ 8.06 (m, 1, -$\overset{|}{\underset{|}{C}}$-H) and τ 8.94 (d, 6, J =

6 cps, gem-dimethyl groups). An analytical sample prepared by

two recrystallizations from methanol had m.p. 92.5-93.5°.

Anal. Calculated for C$_{10}$H$_{12}$N$_2$O$_4$S$_2$: C, 41.65; H, 4.20;

N, 9.72. Found: C, 41.53; H, 4.18; N, 9.58.

t-Butyl 2,4-dinitrophenyl disulfide was obtained in 80% yield

m.p. 128-129° (methanol), [lit. (66) m.p. 126-127°]; nmr (CDCl$_3$)

τ 1.07 (d, 1, aromatic H$_3$), τ 1.61 (nine resonances, 2, aromatic H$_5$

and H$_6$) and τ 8.63 (s, 9, t-butyl).

QUANTITATIVE PRODUCT ANALYSIS

The ampoule containing the reaction mixture was frozen in

liquid nitrogen, opened and analyzed by glpc (model 600-D, 20'
SF-96 at 50°) for iso-butyl and t-butyl chloride. Molar yields were
calculated using Freon 112 as the internal standard and are summar-
ized in Table VII. After analysis the alkyl chlorides and solvent
were removed and the residue was analyzed for polysulfides by either
the nmr or reduction methods described previously.

For analysis by nmr anisole was used as the standard. Peak
enhancement using di-t-butyl disulfide, di-t-butyl tetrasulfide and
di-iso-butyl disulfide as model compounds allowed assignment of all
portions of the spectrum except for three small peaks (about 5% of
total) centered at τ 8.35. These peaks were tentatively assigned
to the methyl groups on a double bond, i.e., of

$$\begin{array}{ccc} H_3C \diagdown & & S \text{---} \\ & C = C \diagup & \\ H_3C \diagup & & \diagdown H \end{array}$$
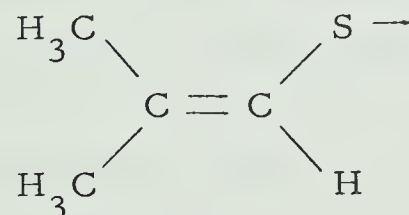
This assignment was in agreement with the presence of a weak band
at 1660 cm^{-1} in the IR spectrum of the polysulfides. This component
of the mixture was not included in the yield calculations described
below.

Singlets for t-butyl protons were present at τ 8.71 (disulfide)
and τ 8.62 (polysulfides). The gem-dimethyl doublet was at τ 9.0,
a multiplet for the tertiary hydrogens was at τ 7.4-8.2 and a multi-
plet for the α-protons was at τ 7.05-7.35 for the iso-butyl groups.
The chemical shifts of the α-protons and the t-butyl singlets were
in agreement with literature values (51, 68).

The isomer ratio was determined by comparing the integrated area for the gem-dimethyl doublet to that for the t-butyl singlets. The total yield of butyl groups was determined by comparing their nine proton signals to the eight proton signals of the anisole. The results are summarized in Table VII.

For reduction of the polysulfides the method used was that previously described for analyzing the polysulfides from the butane reactions. The order of elution during analysis by glpc was Freon 113, t-butyl mercaptan, THF and iso-butyl mercaptan. The mercaptans were identified by comparison of retention times with authentic materials. The results are presented in Table VII.

VIII.   DIRECT ANALYSIS OF POLYSULFIDE COMPOSITION: DISPROPORTIONATION OF DI-t-BUTYL TETRASULFIDE.

DICYCLOHEXYL TETRASULFIDE (XII)

Dicyclohexyl tetrasulfide was prepared from cyclohexyl mercaptan (1.20 g, 10.3 mmole) and sulfur monochloride (0.68 g, 5.0 mmole) by the method of Bloomfield (69). Removal of the solvent from the reaction mixture gave 1.5 g (100%) of a pale yellow oil n_D^{20} 1.6038, lit. (69) n_D^{20} 1.6050. The material was used without further purification. Several analytical methods were investigated to serve as a means of identifying XII as a reaction product from sulfur monochloride and cyclohexane. Both XII and dicyclohexyl disulfide possessed the same R_f when subjected to analysis by tlc (Skellysolve B). Both materials possessed identical IR spectra

with respect to the position of absorption bands. A parent ion could

not be obtained fro XII when subjected to mass spectral analysis.

For these reasons this approach was not pursued further.

DI-t-BUTYL TETRASULFIDE (XIII)

Di-t-butyl tetrasulfide was prepared by the method of Bloom-

field (69) from t-butyl mercaptan (0.96 g, 10.6 mmole) and sulfur

monochloride (0.68 g, 5.0 mmole). Removal of the solvent from

the reaction mixture gave 1.2 g (100%) of a pale yellow oil n_D^{20}

1.5654, lit. (70) n_D^{20} 1.5660. The nmr spectrum (CCl_4) of this

material had a large singlet at τ 8.61 for di-t-butyl tetrasulfide

and a very small singlet at τ 8.71 for di-t-butyl disulfide (2-3%).

Literature values (51) for the chemical shifts of di -t-butyl tetra-

sulfide and di-t-butyl disulfide are τ 8.63 and τ 8.73 respectively.

HIGH RESOLUTION NUCLEAR MAGNETIC RESONANCE ANALYSIS
OF THE POLYSULFIDES FROM REACTION OF SULFUR MONO-
CHLORIDE AND ISOBUTANE

The t-butyl portion of the nmr spectrum (CCl_4) of a represent-

ative sample of the polysulfides obtained from reaction of sulfur

monochloride with isobutane was examined using a 100 mc nmr

spectrometer operating at a sweep width of 100 cps. Under this high

resolution the chemical shifts could be assigned for eleven different

polysulfides. The resonance signals appeared as singlets from τ

8.48-8.65 with the chemical shift (τ) decreasing with an increasing

number of sulfur atoms in the polysulfide chain. The theoretical

reasons for this property of polysulfides have been discussed by Van Wazer and Grant (71). Two series of polysulfides were discernible by this method: di-t-butyl polysulfides and t-butyl-iso-butyl polysulfides. The latter series was displaced 0.012-0.016 τ units downfield from the former. The singlets from di-t-butyl disulfide and di-t-butyl tetrasulfide were located by adding these authentic materials to the polysulfide mixture and reobtaining the spectrum (peak enhancement). The chemical shifts (τ) and the difference in chemical shift ($\Delta \tau$ *) for adjacent members in the series are summarized in Table XII and are compared to the values of obtained by Grant and Van Wazer (51) to lend support to the assignments made. The downfield shift for the t-butyl-iso-butyl polysulfides relative to the corresponding di-t-butyl polysulfides could be explained by the smaller electron releasing effect of a primary carbon atom (iso-butyl group) as compared to a tertiary carbon atom (t-butyl group). An estimate of the mole fraction of each polysulfide relative to the others could be made by a comparison of the peak heights of the singlets. These results are summarized in Table VIII.

PHOTOLYSIS OF DI-t-BUTYL TETRASULFIDE (XIII) FOLLOWED BY NUCLEAR MAGNETIC RESONANCE

The method used by Pickering, Saunders and Tobolsky (52) to follow the thermal disproportionation of dimethyl tetrasulfide by nmr

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* $\Delta \tau$ is defined as $\tau_{(RS_xR)}$ - $\tau_{(RS_{x+1}R)}$

TABLE XII

CHEMICAL SHIFTS[a] FOR THE t-BUTYL GROUPS OF DI-t-BUTYL POLYSULFIDES AND t-BUTYL- iso-BUTYL POLYSULFIDES.

RS$_m$R[b]						RS$_n$R'[b]
m	τ	$\Delta\tau$[c]	$\Delta\tau$[c]	τ	$\Delta\tau$[c]	n
			Ref. 51			
2	8.646	0.077	0.069	8.630	0.076	2
3	8.569	0.034	0.031	8.554	0.031	3
4	8.535	0.012	0.013	8.523[d]	0.012	4
5	8.523[d]	0.010	0.011	8.511[e]	0.012	5
6	8.513	0.009	0.008[f]	8.499[e]		6
7	8.504					

a Chemical shifts are in τ units relative to tetramethylsilane (τ = 10.000).

b R equals t-C$_4$H$_9$; R' equals iso-C$_4$H$_9$

c Defined in text.

d Coincident singlets.

e Appeared as shoulders on the downfield side of the two singlets at τ8.513 and τ8.504 respectively.

f Extrapolated value.

was employed to follow the photolysis of di-t-butyl tetrasulfide. The

following were placed in a clear Pyrex nmr tube: XIII (0.035 g,

0.14 mmole), t-butyl chloride (20 μl for internal reference), carbon

tetrachloride (0.5 ml) and a small, sealed, degassed capillary tube

containing benzene (external reference). After the nmr tube was

degassed and sealed the spectrum was obtained immediately (100 mc,

50 cps sweep width). The tube was then irradiated at 40° and

removed at various intervals for spectral analysis. The chemical

shifts for the polysulfides (relative to t-butyl chloride as τ 8.42) were:

di-t-butyl pentasulfide τ 8.61; tetrasulfide, τ 8.62; trisulfide τ 8.65;

disulfide τ 8.73. The differences in chemical shift ($\Delta \tau$) were in

agreement with those previously observed. The concentration of di-t-

butyl disulfide did not increase over that originally present in the reaction

mixture at zero time. After 150 hr of irradiation small amounts of

di-t-butyl tri- and pentasulfide were present in the reaction mixture,

and the extent of disproportionation estimated from the integrated areas

was about 5%.

IX.   COMPETITION EXPERIMENTS

For the competition experiments, 2 ml portions of a solution

of cyclohexane (2.8 M, 5.6 mmole), the second hydrocarbon (2.7-2.9 M,

5.4-5.8 mmole) and Freon 112 (3 M) were pipetted into two ampoules

containing sulfur monochloride (0.42 g, 3.1 mmole) and one ampoule

containing no sulfur monochloride (the blank). The ampoules were

degassed and sealed under vacuum. The blank was analyzed by glpc

(model 202, 10' SE-30 at 80°, 40 ml He/min) to give the initial peak area ratio of Freon 112 (F_{112}) to cyclohexane (C_6H_{12}) and to the second hydrocarbon (RH). The two ampoules containing sulfur mono-chloride were irradiated at 40° for 60-85 hr. The reaction mixtures were then analyzed by glpc (model 202, 10' SE-30 programmed from 80-200°, 40 ml He/min) to give the final peak area ratios. Relative reactivities ($k_{RH}/k_{C_6H_{12}}$) were calculated from the formula

$$\frac{k_{RH}}{k_{C_6H_{12}}} = \frac{\log \dfrac{(F_{112}/RH)_f}{(F_{112}/RH)_i}}{\log \dfrac{(F_{112}/C_6H_{12})_f}{(F_{112}/C_6H_{12})_i}}$$

where the ratios F_{112}/C_6H_{12} and F_{112}/RH are the peak area ratios obtained by glpc and the subscripts i and f refer to the initial and final ratios. The general formula for calculating relative reactivities is described in the Appendix.

Relative reactivities were determined for cyclohexane, cyclo-pentane, 2,3-dimethylbutane, toluene and norbornane. The results are summarized in Table IX.

X. CYCLOHEXYLTHIOSULFENYL CHLORIDE AS AN INTER-MEDIATE IN THE REACTION OF SULFUR MONOCHLORIDE WITH CYCLOHEXANE.

PREPARATION OF CYCLOHEXYLTHIOSULFENYL CHLORIDE (VI)

Sulfur dichloride was purified by the method of Brauer (72) and

had b.p. 57-58° (700 mm). Cyclohexylthiosulfenyl chloride was prepared by the method Müller and Schmidt (10) from cyclohexyl mercaptan (16.4 g, 0.141 mole) and excess sulfur dichloride (125 ml). After removing the solvent and excess sulfur dichloride under vacuum (10^{-2} mm) the yield of orange oil was 26.0 g (99%).

Molecular weight (iodometric titration). Calculated for $C_6H_{11}ClS_2$ 182.7. Found 182.

The uv spectrum (4.59 x 10^{-4} M in C_6H_{12}) had absorption maxima at 220 (log ϵ 3.12) and 280 mμ (log ϵ 3.39). The spectrum of a more concentrated solution (5.74 x 10^{-2} M) showed no absorption above 520 mμ, demonstrating the absence of sulfur dichloride.

N,N-DIMETHYLCYCLOHEXYLTHIOSULFENAMIDE (XIV)

N,N-Dimethylcyclohexylthiosulfenamide was prepared from cyclohexylthiosulfenyl chloride (5.6 g, 0.031 mole) and dimethyl-amine by the method of Müller and Schmidt (10). After distillation of the crude product under reduced pressure 1.6 g (27%) of XIV was obtained b.p. 70-72° (0.3 mm), n_D^{24} 1.5316; lit. (10) b.p. 54-56° (0.06 mm), n_D^{20} 1.5338.

ATTEMPTED ISOLATION OF XIV FROM A SULFUR MONOCHLORIDE-CYCLOHEXANE REACTION MIXTURE

Two degassed 25 ml portions of a carbon tetrachloride solution of sulfur monochloride (0.44 M, 0.022 mole) and cyclohexane (4.6 M, 0.23 mole) were irradiated at 40° in sealed ampoules until the yellow color had deepened substantially (22 hr). The contents of the ampoules

were combined and added dropwise to dimethylamine (5 g) in carbon tetrachloride (50 ml) cooled to 10°. After addition was complete, the dimethylamine was filtered from the carbon tetrachloride solution. Removal of the solvent from the filtrate left 2.7 g of yellow oil. Distillation of this oil under reduced pressure gave 0.8 g (19%) of impure XIV b.p. $65-70^{\circ}$ (0.1 mm), n_D^{22} 1.5418. A forerun of 0.3 g b.p. $32-33^{\circ}$ (0.25 mm), n_D^{22} 1.5207 was probably the bisdimethyl-amino derivative of sulfur monochloride.

When the impure XIV was analyzed by tlc at least four impurities could be detected, one of which possessed the same R_f as dicyclohexyl disulfide (5-10%). The major component (about 80%) had R_f identical to authentic XIV. A mass spectrum of the product showed a parent ion for XIV at m/e 191 ($C_8H_{17}NS_2$ = 191). Other fragments appeared at m/e 44 (CH_3NCH_3), m/e 64 (S_2) and m/e 83 (C_6H_{11}) and the base peak was at m/e 42 (C_3H_6). A small parent ion for dicyclohexyl disulfide was observed at m/e 230.

REACTION OF CYCLOHEXYLTHIOSULFENYL CHLORIDE WITH CYCLOHEXANE

Degassed carbon tetrachloride solutions of cyclohexylthio-sulfenyl chloride (0.25 M) and cyclohexane (2.8 M) were irradiated at 40° in sealed Pyrex ampoules for 26 hr, after which time completion of reaction could be shown by a negative test for active chlorine with potassium iodide-starch paper. Cyclohexyl chloride and dicyclohexyl disulfide were observed when the reaction mixtures were analyzed

by glpc (model 202, 5' SE-30 programmed from 90-200°, 60 ml He/min). Cyclohexyl chloride was identified by comparison of retention time with authentic material on two columns (above column and model 600-D, 25' UCON POLAR at 120°). Dicyclohexyl disulfide was identical to authentic material with respect to glpc retention time, and mass and IR spectra of samples isolated by preparative glpc.

Two components of retention times similar to those of III and IV previously observed in the sulfur monochloride-cyclohexane reaction mixtures were also present in these reaction mixtures. The mass spectrum of the first component (III) isolated by preparative glpc was the same as that of material previously isolated from sulfur monochloride-cyclohexane reaction mixtures. The second component was present in too low yield to enable isolation.

Three reaction mixtures were analyzed for hydrogen chloride yield by the usual method. The hydrogen chloride was titrated iodometrically. The results are summarized in Table X.

Three reaction mixtures were analyzed by glpc (model 202, 5' SE-30 programmed from 90-200°, 60 ml He/min) for cyclohexyl chloride and dicyclohexyl disulfide using chlorobenzene and naphthalene as external standards. The yields are presented in Table X.

Two reaction mixtures were analyzed by nmr and by reduction to cyclohexyl mercaptan to determine the yield of dicyclohexyl polysulfides. The procedures used were the same as used for analyzing sulfur monochloride-cyclohexane reaction mixtures. The yields are

presented in Table X.

Elemental sulfur (0.032 g, 0.8 equivalent) was added to two 5 ml portions of a carbon tetrachloride solution of VI (0.25M, 1.25 mmole) and cyclohexane (2.8 M, 14 mmole). After degassing, the reaction mixtures were irradiated at 40° for 36 hr, then analyzed for yields of cyclohexyl chloride, dicyclohexyl disulfide and dicyclohexyl polysulfides by the same methods as described above. The yields are summarized in Table X.

XI.   SYNTHETIC REACTION WITH NEOPENTANE

Neopentane (6 ml) and a carbon tetrachloride solution (10 ml) of sulfur monochloride (0.29 M, 2.9 mmole) were placed into five large ampoules. One of these ampoules contained Freon 112 (0.133 g, 0.65 mmole) as the internal standard. The ampoules were degassed, sealed and irradiated at 40° for 3 days after which time the reaction mixtures were nearly colorless and were shown to be free from active chlorine by a negative test with potassium iodide-starch paper.

The reaction mixture containing Freon 112 was analyzed by glpc (model 600-D, 25' UCON POLAR at 40°) in order to estimate the yield of neopentyl chloride. Using calibration data for Freon 112 vs. iso-butyl chloride, a yield of 36% (0.11 g, 1.05 mmole) of neo-pentyl chloride was estimated.

The solvent was removed from all five reaction mixtures and the combined polysulfides were reduced with lithium aluminum hydride (1.0 g, 0.026 mole) in ether (75 ml, heated under reflux for 24 hr).

After decomposition of excess hydride the ether solution was poured into ice-water (100 ml) containing hydrochloric acid (10 ml). The layers were separated, the aqueous portion was extracted with ether (50 ml) and the combined ether extracts were washed with water (50 ml) and saturated sodium chloride solution (50 ml), and dried over anhydrous sodium sulfate. The ether was removed by distillation through a short Vigreux column. Distillation of the residue gave 0.70 g (46%) of neopentyl mercaptan (XV) b.p. 95-100° (688 mm), n_D^{20} 1.4689; IR (CS_2) 2950, 2920, 2905, 2855, 1380 and 1355 cm^{-1} (C-H); nmr (CCl_4) τ 7.63 (d, 2, J = 9 cps, -S-CH_2-), τ 8.88 (t, 1, J = 9 cps, S-H) and τ 9.03 (s, 9, t-butyl). No S-H stretching band was observed in the IR spectrum (2550-2600 cm^{-1}).

The 2,4-dinitrobenzenesulfenyl derivative was prepared from XV (0.19 g, 1.8 mmole) and 2,4-dinitrobenzenesulfenyl chloride (0.445 g, 1.9 mmole) by the usual method (66). After crystallization of the crude product from methanol, 0.35 g (69%) of neopentyl 2,4-dinitrophenyl disulfide m.p. 85-88° was obtained. Two further crystallizations from methanol gave an analytically pure sample m.p. 91-92°.

Anal. Calculated for $C_{11}H_{14}N_2O_4S_2$: C, 43.69; H, 4.67; N, 9.27. Found: C, 43.46; H, 4.81; N, 9.28.

XII.   SYNTHETIC REACTION OF SULFUR MONOCHLORIDE WITH

ADAMANTANE.

SYNTHETIC REACTION: 1-CHLOROADAMANTANE AND 2-CHLORO-

ADAMANTANE

The synthetic reaction was carried out in the same apparatus

as that used for the synthetic reaction with cyclopentane.   Adaman-

tane (20 g, 0.147 mole) was reacted for 4 days with sulfur mono-

chloride (2.00 g, 0.0148 mole) in carbon tetrachloride (100 ml).   The

heat from the lamps (2 x 200 w) maintained a temperature of $50-60^{\circ}$

in the reaction vessel.   The reaction was shown to have gone to

completion by a negative test for active chlorine with potassium

iodide in aqueous acetic acid.   Removal of the solvent from the

reaction mixture left a pale yellow solid which consisted of at least

five products in addition to elemental sulfur and unreacted adamantane

when analyzed by tlc (benzene solvent, plates developed in an iodine

chamber).   This solid was subjected to column chromatography on

a column of one pound of alumina packed in Skellysolve B.   Elution

with Skellysolve B gave 15.3 g of recovered adamantane identified by

R_f on tlc analysis and glpc retention time (model A90-P3, 5' SE-30

at 160°, 60 ml He/min).   Further elution with Skellysolve B gave

2.05 g of material (XVI) as a white solid with a yellow contaminant.

The last of the material (1.58 g) was eluted as a pale yellow oil (XVII)

using chloroform and ethyl acetate as eluants.

Mixture XVI was purified by a solvent separation using acetone.

The insoluble portion (0.27 g) was identified as elemental sulfur by R_f

upon analysis by tlc. The soluble portion (1.61 g) was shown to possess an nmr spectrum $(CDCl_3)$ consistent with a 60 : 40 mixture of 1-chloroadamantane and 2-chloroadamantane by comparison with published spectral data for these two compounds (73, 74). The yields of 1-chloroadamantane and 2-chloroadamantane calculated were therefore 38% (5.6 mmole) and 26% (3.8 mmole) respectively based on sulfur monochloride. The isomers could be separated by preparative glpc. 1-Chloroadamantane had m.p. 168-169°; lit. (75) m.p. 168.5-169.5°; mass spectrum m/e (relative intensity) 172 (3), 170 (8), 136 (10), 135 (100), 93 (9), 79 (11). The nmr spectrum $(CDCl_3)$ of the material was identical to that reported in the literature (73). 2-Chloroadamantane had m.p. 196-197°; lit. (76) m.p. 196°; mass spectrum m/e (relative intensity) 172 (6), 170 (8), 135 (32), 134 (100), 93 (23), 92 (29), 91 (14), 80 (16), 79 (33), 67 (14). The nmr spectrum of this material was identical to that reported in the literature (74).

LITHIUM ALUMINUM HYDRIDE REDUCTION OF XVII: 1-ADAMANTYL MERCAPTAN (XVIII) AND 2-ADAMANTYL MERCAPTAN (XIX).

A portion (1.32 g) of the polysulfides (XVII) previously obtained by column chromatography was reduced with lithium aluninum hydride (1.0 g, 0.026 mole) in THF (50 ml, heated under reflux for 3 hr). After decomposition of excess hydride, the reaction mixture was poured into ice-water (300 ml) containing sulfuric acid (10 ml). After extraction with chloroform (2 x 150 ml), the combined extracts

were washed with water (2 x 150 ml) and dried over anhydrous sodium

sulfate.   Removal of the solvent gave 1.04 g of a pale yellow semi-

solid.   This material was subjected to column chromatography on

a column of 30 g of alumina packed in Skellysolve B.   Elution with

Skellysolve B gave 0.585 g of material consisting of two components

by glpc analysis (model A90-P3, 5' SE-30 at 160°, 60 ml He/min).

The isomer of shorter retention time (XVIII) was the 1-isomer (30%)

and the isomer of longer retention time (XIX) was the 2-isomer (70%).

Using the yield of isolated material and the isomer ratio from glpc

analysis the yield of 1-adamantyl mercaptan was 9% (1.3 mmole) and

the yield of 2-adamantyl mercaptan was 21% (3.1 mmole) based on

sulfur monochloride and corrected to reduction of all of XVII.

Pure samples of the two mercaptans were isolated by prepar-

ative glpc. 1-Adamantyl mercaptan (XVIII) had m.p. 95-97°;   lit.

(77) m.p. 100-102°;   IR (CCl_4) 2910, 2850, 1450 (C-H) and 2565 cm^{-1}

(S-H, weak);   nmr (CCl_4) τ 8.06 (s, 9, β and γ hydrogens), τ 8.29

(s, 6, δ hydrogens) and τ 8.57 (s, 1, S-H);   mass spectrum m/e

(relative intensity) 168 (14), 136 (12), 135 (100), 93 (15), 79 (17).

Molecular weight (exact mass).   Calculated for $C_{10}H_{16}S$

168.0973.   Found 168.0970.

2-Adamantyl mercaptan (XIX) had m.p. 146-148°;   IR (CCl_4)

2910, 2850, 1465, 1455 (C-H) and 2580 cm^{-1} (S-H, very weak);   nmr

(CCl_4) τ 6.65 (d broad, 1, J = 7 cps, -S-$\overset{|}{\underset{|}{C}}$-H), τ 7.77 and 8.48

(q broad, 4, $J_{\underline{gem}}$ = 13 cps, A_2B_2 quartet) τ 8.15 (s broad, 10) and

τ 8.54 (d, 1, J = 7 cps, S-H);   mass spectrum m/e (relative intensity)

168 (33), 136 (15), 135 (100), 93 (20), 91 (11), 81 (10), 79 (21).

Molecular weight (exact mass). Calculated for $C_{10}H_{16}S$ 168.0973. Found: 168.0974.

The A_2B_2 quartet in the nmr spectrum of XIX was examined further by spin decoupling at 100 mc. Irradiation of the upfield protons caused the doublet of the downfield protons to collapse into a singlet and vice versa. This A_2B_2 pattern is a general feature of the nmr spectra of 2-substituted adamantanes and was first investigated by van Deursen and Korver (74).

1-ADAMANTYL 2,4-DINITROPHENYL DISULFIDE AND 2-ADAMANTYL 2,4-DINITROPHENYL DISULFIDE

1-Adamantyl mercaptan (0.011 g, 0.06 mmole) was reacted with 2,4-dinitrobenzenesulfenyl chloride (0.015 g, 0.06 mmole) in the usual manner. After crystallization of the product from methanol 0.013 g (59%) of 1-adamantyl 2,4-dinitrophenyl disulfide was obtained as yellow needles m.p. 159-160°.

Anal. Calculated for $C_{16}H_{18}N_2O_4S_2$: C, 52.44; H, 4.95; N, 7.65. Found: C, 52.23; H, 4.94; N, 8.10.

2-Adamantyl mercaptan (0.025 g, 0.15 mmole) was reacted with 2,4-dinitrobenzesulfenyl chloride (0.038 g, 0.16 mmole). The crude product was crystallized from ethyl acetate-cyclohexane. After a further crystallization from methanol 0.018 g (33%) of analytically pure 2-adamantyl 2,4-dinitrophenyl disulfide m.p. 144-145° was obtained.

<u>Anal.</u> Calculated for $C_{16}H_{18}N_2O_4S_2$:   C, 52.44; H, 4.95;

N, 7.65.   Found: C, 52.78; H, 5.26; N, 7.33.

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APPENDIX

The methods used in this thesis for calculating selectivities and relative reactivities are outlined below.

1. Selectivities

Selectivity calculations can be illustrated most simply by means of a sample calculation. For example, one reaction of pentachlorobenzenesulfenyl chloride with isobutane (page 26, Table III, run 13) gave the following relative yields (mole/mole) of primary (1°) and tertiary (3°) substitution products.

|	product	yield
1°	iso-C_4H_9Cl	0.01
1°	iso-$C_4H_9SC_6Cl_5$	0.19
3°	t-C_4H_9Cl	0.15
3°	t-$C_4H_9SC_6Cl_5$	0.39

The yield of tertiary products (0.15 + 0.39 = 0.54) relative to the yield of primary products (0.01 + 0.19 = 0.20) is $\frac{0.54}{0.20}$ = 2.7. Since there are nine primary hydrogen atoms and one tertiary hydrogen atom in the isobutane molecule, the tertiary hydrogen is therefore 2.7 x 9 = 24.3 times more reactive than the primary hydrogens. Thus the primary : tertiary selectivity of pentachloro-benzenesulfenyl chloride is 1 : 24.3 in hydrogen atom abstraction.

2. Relative Reactivities

Relative reactivities are the relative rate constants (k_1/k_2) for hydrogen abstraction from two substrates R_1H and R_2H.

$$R_1H + X\cdot \xrightarrow{\ k_1\ } R_1\cdot + HX$$
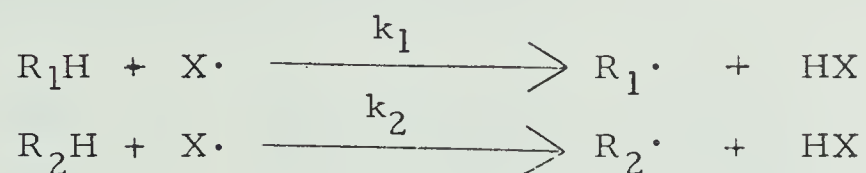
$$R_2H + X\cdot \xrightarrow{\ k_2\ } R_2\cdot + HX$$

$$- \frac{d\,[R_1H]}{dt} = k_1\,[R_1H]\,[X\cdot]$$

$$- \frac{d\,[R_2H]}{dt} = k_2\,[R_2H]\,[X\cdot]$$

$$\frac{-\,d\,[R_1H]}{-\,d\,[R_2H]} = \frac{k_1\,[R_1H]\,[X\cdot]}{k_2\,[R_2H]\,[X\cdot]} = \frac{k_1}{k_2}\,\frac{[R_1H]}{[R_2H]}$$

$$\frac{-\,d\,[R_1H]}{[R_1H]} = -\frac{k_1}{k_2}\,\frac{d\,[R_2H]}{[R_2H]}$$

$$- \int_{[R_1H]_i}^{[R_1H]_f} \frac{d\,[R_1H]}{[R_1H]} = -\frac{k_1}{k_2} \int_{[R_2H]_i}^{[R_2H]_f} \frac{d\,[R_2H]}{[R_2H]}$$

The subscripts refer to the initial (i) and final (f) concentrations of R_1H and R_2H. Integration of this expression gives

$$- (\ln\,[R_1H]_f - \ln\,[R_1H]_i) = -\frac{k_1}{k_2}\,(\ln\,[R_2H]_f - \ln\,[R_2H]_i)$$

so $\qquad \dfrac{k_1}{k_2} = \dfrac{\ln [R_1H]_i - \ln [R_1H]_f}{\ln [R_2H]_i - \ln [R_2H]_f}$

or using logarithms to the base ten

$$\dfrac{k_1}{k_2} = \dfrac{\log ([R_1H]_i / [R_1H]_f)}{\log ([R_2H]_i / [R_2H]_f)}$$

What is required experimentally therefore, is some measure of $[R_1H]_i / [R_1H]_f$ and $[R_2H]_i / [R_2H]_f$. These ratios can often be conveniently found by means of gas liquid partition chromatography, but any analytical method which provides these ratios can be used.